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A Study to Evaluate Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery

Harmon Engineering and Testing
Auburn, AL

Prepared for

Environmental Monitoring Systems Lab.
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A STUDY TO EVALUATE CARBON MONOXIDE AND HYDROGEN SULFIDE CONTINUOUS EMISSION MONITORS AT AN OIL REFINERY

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An eleven month field evaluation was done on five hydrogen sulfide and four carbon monoxide monitors located at an oil refinery. The hydrogen sulfide monitors sampled a fuel gas feed line and the carbon monoxide monitors sampled the emissions from a fluid cat cracker (FCC). Two of the four carbon monoxide monitors operated over the eleven month period and showed good agreement with the leuco crystal violet (LCV) wet chemical method developed for the purpose of checking monitor accuracy. The LCV method and the special stack gas conditioning system employed to remove moisture and particulate from the FCC stack gas are also described. The gas conditioning system operated for 14 months without a major failure. None of the five hydrogen sulfide monitors was found acceptable. Two of the five never obtained a valid sample and the other three did not agree well with the EPA Reference Method 11 during relative accuracy testing.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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FOREWARD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agencywide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances and the Office of Enforcement.

The following investigation was conducted at the request of the Office of Air Quality Planning and Standards (OAQPS) to determine the performance that can be expected from continuous emission monitors installed at petroleum refineries. The results of this study will be used by the OAQPS to determine the appropriateness of these monitors for use at refineries and to determine reasonable performance specifications for these monitors.

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) has promulgated New Source Performance Standards (NSPS) that require petroleum refineries to continuously monitor the carbon monoxide (CO) emissions from fluid catalytic cracking (FCC) units and also to continuously monitor either the hydrogen sulfide (H_2S) concentration in fuel gas feed lines or the resulting sulfur dioxide (SO_2) concentration in the boiler exhaust. However, refineries are not required to install H_2S or CO continuous emission monitors (CEMs) until performance specifications have been published by the EPA. Tentative performance specifications, proposed by EPA after laboratory and short-term field evaluations, were extensively evaluated in a year-long field evaluation conducted using five H_2S and four CO continuous emission monitors. The H_2S CEMs were installed on a fuel gas line and the CO CEMs were installed on a stack from a FCC unit at an east coast refinery. During the evaluation, performance specification testing was routinely performed on the instruments as the instruments were operated and maintained in a work environment. The CO CEMs were generally reliable and able to meet proposed performance specifications. The H_2S CEMs were not able to meet the proposed relative accuracy criteria but the difference in measured concentration could not be isolated to the CEMs or the reference method.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AA	— Applied Automation
CEM	— continuous emission monitor
d.c.	— direct current
EPA	-- Environmental Protection Agency
FCC	-- fluid catalytic cracker
FID	— flame ionization detector
FPD	-- flame photometric detector
FS	— full scale
GC	-- gas chromatograph
HAI	-- Houston Atlas, Incorporated
ID	— inside diameter
IR	— infrared
LCV	-- leuco crystal violet
MSA	-- Mine Safety Appliance
NBS	-- National Bureau of Standards
NDIR	— nondispersive infrared
NSPS	— New Source Performance Standards
OD	— outside diameter
PAI	— Process Analyzers, Incorporated
ppm	— parts per million
PST	-- Performance Specification Test
PVC	— polyvinyl chloride
RA	-- relative accuracy

SYMBOLS

CH_4	— methane
CH_3SH	— methyl mercaptan
CO	-- carbon monoxide
CO_2	— carbon dioxide
H_2S	-- hydrogen sulfide
NO_x	— oxides of nitrogen
SO_2	— sulfur dioxide

SECTION 1

INTRODUCTION

On March 15, 1978, EPA promulgated New Source Performance Standards (NSPS) that required petroleum refineries to continuously monitor the carbon monoxide (CO) emissions from fluid catalytic cracking (FCC) units (1). Refineries were required to also continuously monitor either the hydrogen sulfide (H_2S) concentration in fuel gas feed lines or the resulting sulfur dioxide (SO_2) concentration in the boiler exhaust (1). However, refineries were not required to install H_2S or CO continuous emission monitors (CEMs) until performance specifications were published by the EPA.

Tables 1 and 2 present the tentative performance specifications for both CO and H_2S monitors that were subsequently proposed by an EPA contractor after laboratory and short-termed field evaluations. Terms used in these tables and throughout the report are defined in Appendix A.

In the laboratory phase, candidate instruments were evaluated to determine:

- response characteristics
- stability with time, temperature and flow rate
- sensitivity to potential interferences likely to be present in the sampled gas.

The five CO and two H_2S monitors that performed adequately in the laboratory were then evaluated for approximately two months at a petroleum refinery (2,3). Only one CO monitor and one H_2S monitor performed adequately in the field testing. In the case of the CO monitors, daily calibration checks were mandatory for reliable operation of all the instruments, but even with the inclusion of daily calibration, the contractor questioned the long-term reliability of the CO monitors. Further, instrument malfunctions, sampling system malfunctions and data logger malfunctions plagued the field evaluation of both types of monitors which resulted in a significant amount of downtime and lost data.

In April 1979, EPA initiated additional work to determine: (1) information about long-term instrument durability, data validity and maintenance requirements of commercially-available CO and H_2S CEMs at a refinery; and (2) the validity of the tentative performance specifications for the instruments. In addition, a manual (non-instrumental) method for measuring CO was to be developed and evaluated to serve as an alternate to EPA Reference Method 10.

To procure the monitors, EPA contacted vendors of CO and H_2S continuous stack gas monitors by letter and asked them to submit information about the monitor(s) they thought would be suitable for the appropriate refinery process, the operating principle and approximate cost. A copy of that letter and the Project Accomplishment Plan that accompanied it are included in Appendix B. Appendix C contains the vendor response to the letter and, if they suggested a monitor, the model number, cost and operating principle.

Of the 35 vendors contacted, 16 did not respond. A total of 10 H_2S and 13 CO monitors were recommended for consideration. From this list, five H_2S and four CO monitors were selected for evaluation. The pertinent information about each instrument is included in Tables 3 and 4. The selection criteria (described in detail in Appendix B) involved total cost, operation/detection principle and engineering judgement about the likelihood the monitor would be suitable for the application. For example, one company proposed to use a converted NO_x monitor for measuring H_2S, but did not consider the likelihood that organics in the fuel gas would interfere with the chemiluminescence reaction.

After receipt, the monitors were installed in a trailer at the Harmon Engineering & Testing (HE&T) facility in Auburn, Alabama and were subjected to checks for: drift, response time, electronic noise level, interferences and response variation due to changes in ambient temperature and sample flow rate. The monitors and trailer were then transported to a refinery for an 11-month field study in which they were tested at periodic intervals for relative accuracy, response time, calibration error and drift.

The refinery at which the field evaluation was conducted had added a new CO boiler to the FCC unit in early 1979 to recover additional energy from the FCC exhaust gas and to reduce the CO concentration in the gas stream. The emission gas from this unit was used for the CO CEM evaluation.

An EPA-designed sample conditioning system (described in Appendix D) removed the moisture and particulate matter from the FCC gas at the sampling port. The conditioned gas was transported to the sample manifold through 200 meters of 0.95 cm ID black, nylon tubing at a flow rate ranging from 8 to 15 Lpm. This sample conditioning system was installed in February 1980, and was operated continuously for eleven weeks before the monitors arrived at the refinery to allow time to correct any potential design deficiencies (none were found) before attaching the monitors to it. Three measurements of CO_2 and CO concentrations performed during this 11 week period indicated these compounds were not affected by the sample conditioning system. In these checks, inlet and outlet samples were taken in Tedlar bags and analyzed by NDIR techniques.

A sample manifold was used to distribute the conditioned FCC stack gas to the four CO CEMs. The distribution system was designed to vent excess gas not required by the instruments for normal operation. The unit was also equipped with solenoid valves controlled by a data logger for automatic zero and span checks each day.

The H_2S monitors sampled a fuel gas line at a point downstream of the amine treater used to remove H_2S from the fuel gas. During the project, both monoethanolamine and diethanolamine were used in the amine treater.

The fuel gas was distributed to the five H_2S monitors by means of a six-port sampling manifold that was supplied continuously with treated fuel gas. The fuel gas was transported from the sampling point to the instrumentation trailer through approximately 100 m of 0.63 cm OD stainless steel tubing.

All instruments were located in a 24-foot long, air conditioned trailer. Figure 1 shows the location of the instrumentation trailer in relation to the two sources that were monitored.

The output from the monitors was simultaneously recorded on an Esterline Angus Model PD 2064 data logger, Techtran Model 816 cassette tape recorder and an Esterline Angus multipoint recorder. While sampling process gas, each monitor's output was read at 3-minute intervals and the average value for 10 readings was printed by the data logger and simultaneously recorded by the Techtran Model 816. The multipoint recorder printed each 3-minute reading without averaging. During relative accuracy testing, the data logger measured each monitor's output at 1-minute intervals and reported the average every 20 or 30 minutes.

At the beginning of the field evaluation (April 1980), the tentative performance tests listed in Tables 1 and 2 were performed. Field testing performed after May 1980, however, concentrated on relative accuracy and calibration drift tests in response to a major change in EPA's overall approach to monitor system performance specifications. This change, formally proposed in the Federal Register(4), involved a drastic simplification on the Performance Specification Test (PST) Procedure 4. Under these proposed PST revisions the only mandatory tests are relative accuracy and calibration drift. The other tests that were previously required (5) are now optional.

Five CO and ten H_2S relative accuracy tests were conducted during the 11-month field evaluation, but not all monitors were operational in all tests. In addition, the monitors were subjected to daily 15-minute zero and span checks. Except for days when relative accuracy

testing was being performed, zero and span calibrations were not normally adjusted more often than weekly (frequently less than once per month) in order to provide data on the drift characteristics of each instrument. Only the gas chromatograph (GC) instruments were equipped with automatic zero and no instrument was equipped with automatic span adjustment.

Relative accuracy tests on the H_2S monitors used EPA Method 11 (6) as the reference method. Relative accuracy tests on the CO monitors were conducted using EPA Method 10 and an alternate method (described in Appendix E) developed during this study. This alternate method can be used to check the accuracy of CO continuous monitors using NDIR as the measurement technique.

TABLE 1. TENTATIVE PERFORMANCE SPECIFICATIONS FOR CO CEMS

PARAMETERS	SPECIFICATION
Range	0-1000 ppm
Calibration Error	≤2% Span
Relative Accuracy[1,2]	≤10% Mean Ref. Value
Precision	≤1% Span
Response Time (System)	≤10 Minutes
Output Noise	≤1% Span
Zero Drift, 2 Hours[1]	≤1% Span
Zero Drift, 24 Hours[1]	≤2% Span
Span Drift, 24 Hours[1]	≤2.5% Span
Interference Equiv. 15% CO_2 as ppm CO 10% H_2O as ppm CO	 ≤10 ppm ≤5 ppm
Operational Period	≥168 Hours

[1] Expressed as sum of absolute mean value plus 95% confidence interval in a series of tests.

[2] This value is based on a relative comparison of the monitors to each other and not to Method 10. The terms are defined in Appendix A.

TABLE 2. TENTATIVE PERFORMANCE SPECIFICATIONS FOR H_2S CEMS

PARAMETERS	SPECIFICATION
Range	0-300 ppm
Calibration Error[1]	≤5% of Each Calibration Mixture
Relative Accuracy[1]	≤10% Mean Ref. Value
Response Time (System)	≤15 Minutes
Zero Drift, 2 Hours[1]	<2% Span
Zero Drift, 24 Hours[1]	<2% Span
Span Drift, 2 Hours[1]	<2% Span
Span Drift, 24 Hours[1]	<2.5% Span
Operational Period	≥168 Hours

[1] Expressed as sum of absolute mean value plus 95% confidence interval in a series of tests.

TABLE 3. CO CEMS EVALUATED

INSTRUMENT MANUFACTURER	MODEL NUMBER	ABBREVIATION	OPERATING PRINCIPAL
Anarad, Inc. P. O. Box 3180 Santa Barbara, CA 93105	501R	Anarad	Nondisperaive Infrared Detector (NDIR) Optical Solid State Detector
Ecolyzer Energetics Science 85 Executive Blvd. Division of Becton Dickinson Company Elmsford, NY 10523	3107/2949	Ecolyzer	Electrochemical Sensor
Applied Automation, Inc. Pawhuska Road Bartlesville, OK 74004	Optichrom 102	AA102	Gas Chromatograph/Flame Ionization Detector (GC/FID)
Mine Safety Appliances Company 7522 Neade Street Pittsburgh, PA 15208	LIRA 202	MSA	Nondisperaive Infrared/ Luft Detector (NDIR/Luft)

TABLE 4. H_2S CEMS EVALUATED

INSTRUMENT MANUFACTURER	MODEL NUMBER	ABBREVIATION	OPERATING PRINCIPAL
Bendix Environmental & Process Instrument P. O. Drawer 831 Lewisburg, W. VA 24901	7770	Bendix	Gas Chromatograph/Flame Photometric Detector (GC/FPD)
Del Mar Scientific, Inc. P. O. Box 486 Addison, Texas	DM-W	Del Mar	Lead Acetate Impregrated Paper Tape
Houston Atlas, Inc. 9441 Baythorne Drive Houston, TX 77041	825R/102	HAI	Lead Acetate Impregrated Paper Tape
Process Analyzers, Inc. 1101 State Road Princeton, NJ	32-230	PAI	Gas Chromatograph/Flame Photometric Detector (GC/FPD)
Teledyne Analytical Instruments 333 W. Mission Avenue San Gabriel, CA 91776	611 DHCO-20X	Teledyne	Ultraviolet Absorption

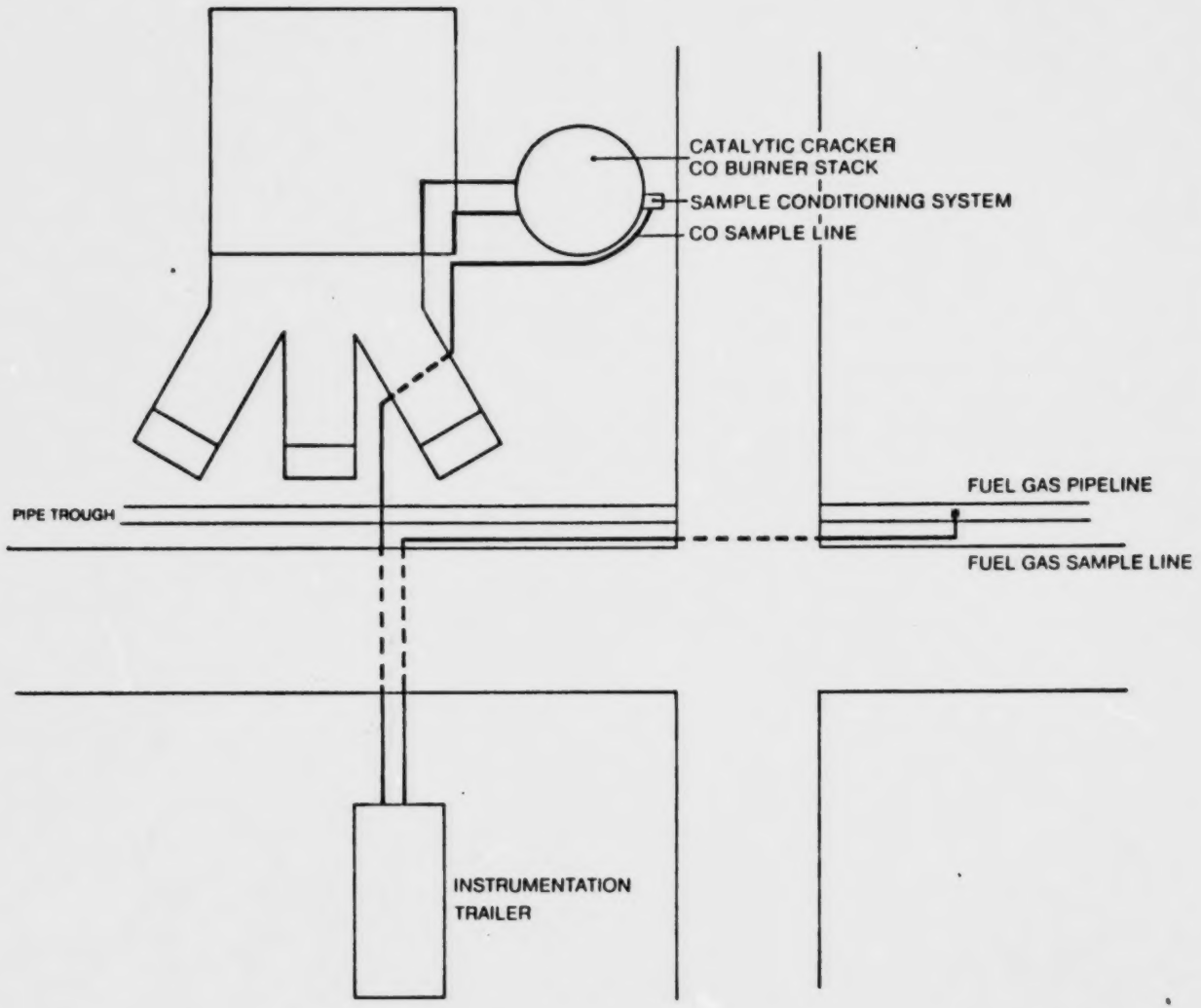

FIGURE 1. SKETCH OF FIELD EVALUATION SITE

SECTION 2

SUMMARY AND CONCLUSIONS

CARBON MONOXIDE MANUAL METHOD

The analytical portion of the manual CO test method developed in this study was biased 4 percent high with respect to a Bendix 8501-5CA NDIR CO analyzer. The precision associated with a single analysis was 4.3 percent of the concentration for the range 10 to 1100 ppm. The precision was approximately 2.5 percent of the mean concentration for analyses performed in triplicate. This means that two analytical results on the same bag sample should differ by more than 8.4 percent only one time in 20 due to chance alone. The method was significantly affected by SO_2 and NO, so these compounds were removed during sample collection by bubbling the gas through alkaline potassium permanganate.

Table 5 summarizes the data collected for each CO instrument during the study. Tables 6 and 7 summarize the relative accuracy and calibration drift tests, respectively. Sometimes, less than the desired nine manual method tests were achieved because of leaking Tedlar bags and process failure. Table 8 shows the effect of CO_2, NO_x and SO_2 on each monitor's response. The following paragraphs summarize the performance of each instrument.

CARBON MONOXIDE MONITORS

Applied Automation Optichrom 102

The monitor performed well in the laboratory checkout, but not in the field evaluation. A valid relative accuracy test was never achieved because of the monitor's erratic performance; thus, its percent uptime was zero.

Ecolyzer 3107

This monitor was equipped with an Energetics Science Model 2949 scrubber to remove NO_x and SO_2. Originally, each scrubber cost $21, but by June 1980, this price had increased to $45. The scrubber was found to be inadequate for long-term use on FCC gases. scrubber failure, which in turn caused monitor detector failure, occurred from 1 to 20 days after installation (depending on the NO_x and SO_2 concentration encountered). To protect the detector and save cost, a

25 cm long by 2.5 cm diameter PVC pipe containing activated charcoal was substituted for the Model 2949 scrubber during routine use and the Model 2949 scrubber used only during relative accuracy tests. The response time of the system with the large charcoal scrubber installed was approximately 30 minutes compared to less than 1 minute when the Model 2949 scrubber was used. At the SO_2 and NO_x concentrations normally encountered in an FCC stack (500 ppm SO_2, 200 ppm NO_x) even a new Model 2949 scrubber was unable to remove all of the interfering gases such that the instrument could pass a relative accuracy test (See RA test 2/81 (A) in Table 6). Carbon dioxide at 15 percent by volume did not interfere. The monitor drifted significantly over a period of several days at frequent intervals. The detector was replaced once during the study and the evaluation stopped after the detector failed the second time. Detector failure was also a problem in the previous study (2). This instrument does not appear to be suitable to continuously monitor CO concentrations in FCC emissions.

Mine Safety Appliance (MSA) Lira 202

As received, the output from this monitor was not compatible with the data logger thus, the laboratory check-out tests were not completed before the trailer was sent to the refinery. At the refinery the monitor drifted on a daily basis but, over a month, the zero and span drift frequently averaged out to less than 3 percent. No interference was found from SO_2 or NO_x and only a small and constant interference was found from CO_2 (1 ppm per 1 percent CO_2). Although the test was not done, water vapor would not be expected to be a significant interferent. The monitor successfully completed the 11-month evaluation with only two failures, both of which were corrected by an optical realignment.

Anarad 501-R

Except for the time it was in transit to the refinery, this monitor operated continuously without an outage from October, 1979 until testing was completed in April 1981. Interferences from SO_2 and NO_x were not experienced, but small, constant interferences did result from CO_2 (3 ppm per 1 percent CO_2) and from water (3 ppm per 1 percent H_2O). Since the stack gas was conditioned to yield a dewpoint of $-20^{\circ}C$, water was not an interferent in the field tests. The monitor's output was usually more stable than any of the other instruments.

HYDROGEN SULFIDE MONITORS

The H_2S CEMs were evaluated in the laboratory prior to the field testing. Table 9 summarizes the data collected for each H_2S instrument during the study. Table 10 summarizes the relative accuracy testing performed in the field, and Table 11 summarizes the

calibration drift tests. In some relative accuracy tests, less than nine reference method samples were collected because plant upsets increased the H_2S concentration above the span range of the monitors.

The following paragraphs summarize the performance of each instrument.

Bendix Model 7770

This monitor operated continuously from initial start-up until final shut-down with only four brief outages. Two outages were caused by a ruptured diaphragm in the sampling valve, one outage occurred when an operator accidently shorted a circuit in the heater control unit and the fourth occurred from an obstruction in the process air supply.

Interferences were not detected during the initial checkout. However, during relative accuracy tests, a possible interference from something in the fuel gas was indicated but could not be confirmed. Since the monitor sampled the fuel gas once every 3.5 minutes, it was difficult to conduct a relative accuracy test when the H_2S level in the fuel gas was changing rapidly (as frequently occurred). The instrument generally performed in a reliable manner throughout the evaluation.

Process Analyzers Incorporated Model 32-230

This monitor operated for less than 3 days during the laboratory check-out and was returned to the manufacturer for repairs on three separate occasions. Mechanical failure, electronics failure and corrosion of parts prevented the monitor from obtaining a valid analysis of the fuel gas and thus its percent uptime was zero. The instrument does not appear suitable for use in this application.

Teledyne Model 611 DMCO-20X

This monitor was received approximately 3 months later than scheduled, which prevented a complete laboratory checkout of the monitor. A valid analysis of the fuel gas was never obtained because of interference from diethanolamine and sulfur compounds such as mercaptans and carbonyl sulfide. The molecular sieve scrubber originally supplied with the monitor could not compensate for these interferences. By the time Teledyne supplied an improved scrubber, the monitor had ceased to operate; thus its percent uptime was zero. The instrument does not appear to be suitable for use in this application.

Houston Atlas Model 825R/102

Although this monitor suffered frequent mechanical failure, it did complete most of the field testing program. The most frequent cause of failure was the gas dilution system. This is the same problem that affected the Houston Atlas instrument evaluated in a previous study(3). This monitor required a minimum of 4 hours for a major calibration and, at times, was subject to severe drifting. Some of the operational problems encountered were due to operator error and the corrosive environment of the instrumentation trailer. Some data were lost because the person conducting the daily checks failed to replace the lead acetate tape in a timely manner.

Del Mar Scientific Model DM-W

This monitor operated for the entire test program without mechanical failure. However, because rotameters were used to achieve a 1:10 dilution of the fuel gas, its calibration changed when density and viscosity of the fuel gas changed. Sudden changes in the gas viscosity occurred during some of the relative accuracy tests; thus the agreement between Method 11 and the monitor varied drastically during some tests. A bias also seemed to exist between the monitor and the manual method that could not be explained by viscosity changes. Some data were lost because the person conducting the daily checks failed to replace the lead acetate tape in a timely manner.

TABLE 5. DATA SUMMARY OF CO CEMS

	SPECIFICATIONS PROPOSED IN REF. 2	ANARAD	ECOLYZER	MSA	AA102
LABORATORY DATA					
Precision (% FS)	≤1	<0.1	<0.1	<0.1	<0.1
Span Noise (% FS)	≤1	<0.1	<0.6	<0.2	<0.1
Zero Noise (% FS)	[a]	0.5	0.4	0.1	0.9
H_2O Interference (as ppm CO)	≤4	32.4	n/a	[b]	3.0
15% CO_2 Interference (as ppm CO)	≤10	28.2	<0.1	[b]	<0.1
Response Time (seconds)	≤600	7.5	53	4.8	138
FIELD DATA					
Zero Drift, 24 Hr. (% FS)	≤2	2.5	9.2	2.2	0.4
Zero Drift, 2 Hr. (% FS)	≤1	0.89	1.3	1.3	0.42
Span Drift, 24 Hr. (% FS)	≤2.5	4.2	53.8	3.1	4.3
Calibration Error (% FS)	≤2				
- high (% FS)	[a]	1.7	5.0	[b]	2.6[c]
- medium (% FS)	[a]	9.1	13.0	[b]	6.9[c]
- low (% FS)	[a]	4.7	4.6	[b]	8.4[c]
Field Response Time, 90%/95% FS (seconds)	≤600	13/16	45/47	11/13	242/242
Instrument Operational Time[d] (%)	[a]	100	57	86	0

[a] Not specified.

[b] Data not complete due to instrument malfunction.

[c] Result of one test.

[d] Time the instrument was producing useable data during the 11-month field evaluation without considering the absolute accuracy of the data, i.e., without correcting for the days the monitor was out of calibration. However, if the monitor was known to be malfunctioning and not just out of calibration, the monitor was considered to be off line.

TABLE 6. SUMMARY OF CO RELATIVE ACCURACY TESTS AT REFINERY

DATE	NUMBER OF REFERENCE METHOD SAMPLES	MEAN CO_2 CONC (%)	LCV[a] CO CONC (ppm)	RELATIVE ACCURACY					
				ECOLYZER		ANARAD[b]		MSA[b]	
				% Std[c]	% [CO]	% Std[c]	% [CO]	% Std[c]	% [CO]
9/80	5	2	80	5	34	3.8	24	2.9	18.4
1/81	9	2	404	14	17	13	16	13	16
2/81 (A)	9	12	507[d]	>100	>100	7.7	7.6	4.2	4.3
2/81 (B)	9	3	712	[e]	[e]	12.7	8.9	9.7	6.8
Mean				40	50	9.3	14	7.4	11

[a] This is the average of the manual method results using the leuco crystal violet method developed in this study.

[b] Corrected for CO_2 interference.

[c] Standard for CO: 500 ppm.

[d] Monitors sampled cylinder gases containing 502 ppm CO, 12% CO_2 and different concentrations of NO and SO_2 in nitrogen. This was done to evaluate the performance of the monitors when they were sampling a stack gas with NO_x and SO_2 levels representative of an FCC stack gas. During the 11-month study, process upsets and refinery equipment malfunction caused the CO levels to exceed the span range of the monitors and so it was necessary to dilute the stack gas to bring the CO level into the working range of the monitors during the relative accuracy test. Dilution was obtained by introducing plant instrument air at the probe. This dilution reduced the NO_x and SO_2 levels by a factor of 4 to 6 and permitted the Ecolyzer to obtain an accurate analysis of the stack gas.

[e] Monitor not operational because of detector failure from high SO_2 and NO levels encountered in Test 2/81(A).

TABLE 7. CALIBRATION DRIFT TEST RESULTS FOR CO MONITORS

DAY	CALIBRATION DRIFT[a, b] (%)					
	ECOLYZER		ANARAD		MSA	
	Zero	Span	Zero	Span	Zero	Span
Test 1						
1	1.4	0.4	1.7	0.1	0.6	0.1
2	0.3	4.4	0.2	2.4	0.9	1.2
3	0.2	1.7	0.2	1.6	1.2	2.0
4	0.6	1.0	1.0	0.2	1.4	0.8
5	0.4	0.7	2.0	0.8	2.5	6.2
6	0.9	0.9	2.1	1.5	3.3	3.0
7	1.2	1.6	3.2	4.5	2.9	0
Test 2						
1	0.2	7.2	2.4	0.7	0	0.9
2	0.2	0.1	0.2	4.4	1.7	2.4
3[c]	0.7	10.8	0.4	3.4	5.4	1.3
4	0.2	0.2	0.4	0.3	1.3	3.6
5	0	1.6	1.1	0.4	2.5	3.7
6	0.1	0.9	0.1	1.9	0.2	1.1
7	0.1	0.3	0.5	1.0	0.1	1.7
Test 3						
1	0.1	0.1	0.9	0.6	0.2	1.2
2	0.3	3.4	1.3	1.7	0.2	1.2
3	0	0.4	0	0.7	0.4	0.1
4	0.1	0.9	0.6	1.1	0.7	1.2
5	3.1	2.7	0.4	1.1	1.8	2.8
6	2.2	2.8	0.4	0.1	4.2	1.1
7	0.7	0.9	0.2	0.1	0.9	2.8

[a] Values in table represent the daily drift as defined by the following equation

$$\frac{|\text{Calibration Gas Concentration} - \text{Monitor Reading}|}{\text{Monitor Span Value}} \times 100\%$$

[b] Because long-term drift was of primary concern, the instruments were not zeroed daily. The values in the table have been corrected by the daily zero drift.

TABLE 8. EFFECT OF CO_2, NO_x, SO_2 ON CO MONITORS

DATE	[CO] (ppm)	MONITOR RESPONSE (ppm)			MONITOR RESPONSE CORRECTED FOR CO_2 INTERFERENCE[a]		
		Ecolyzer	Anarad	MSA	Ecolyzer	Anarad	MSA
6/5/80	100[c]	165	149	117	165	113	105
9/20/80	100[c]	141	139	112	148	101	100
11/18/80	100[c]	b	152	113	b	116	101
1/20/81	100[c]	206	140	107	206	104	95
2/17/81	500[d]	1680	544	504	1680	508	492
2/17/81	500[e]	1430	538	512	1430	502	500
2/17/81	500[f]	1660	523	504	1660	487	492

[a] CO_2 Interference: Ecolyzer - none; Anarad - 3 ppm/1% CO_2; MSA - 1 ppm/1% CO_2.

[b] Monitor not operational because of detector failure.

[c] Cylinder Analysis: 12% CO_2; 200 ppm NO; 500 ppm SO_2; balance N_2.

[d] Cylinder Analysis: 12% CO_2; 400 ppm NO; 0 ppm SO_2; balance N_2.

[e] Cylinder Analysis: 12% CO_2; 0 ppm NO; 700 ppm SO_2; balance N_2.

[f] Cylinder Analysis: 12% CO_2; 200 ppm NO; 500 ppm SO_2; balance N_2.

TABLE 9. DATA SUMMARY OF H_2S CEMS

	SPECIFICATIONS PROPOSED IN REFERENCE 3	BENDIX	DEL MAR	HAI	PAI	TELEDYNE
LABORATORY DATA						
Precision (% FS)	[a]	0.3	4.3	2.8	[b]	0.6
Span Noise (% FS)	[a]	0.4	1.1	0.9	[b]	0.6
Zero Noise (% FS)	[a]	0.1	2.1	0.5	[b]	2.4
100 % CH_4 Interference (% FS)	[a]	<0.1	<0.1	-0.2	[b]	<1
40% CH_4 in H_2 Interference (% FS)	[a]	<0.1	<0.1	-0.4	[b]	<1
200 ppm CH_3SH Interference (% FS)	[a]	<0.1	<0.1	<0.1	[b]	82
Response Time (sec)	≤900	210	306	630		35
FIELD DATA						
Zero Drift, 24 Hr. (% FS)	≤2	0.04	5.2	1.6	[b]	[b]
Zero Drift, 2 Hr. (% FS)	≤2	0.05	2.1	1.9	[b]	6.1
Span Drift, 24 Hr. (% FS)	≤2.5	1.7	11.7	13.4	[b]	[b]
Span Drift, 2 Hr. (% FS)	≤2	0.6	3.4	13.1	[b]	2.1
Calibration Error (% FS)	≤5					
- high (% FS)	[a]	0.7	9.2[c]	14[c]	[b]	9.3[c]
- medium (% FS)	[a]	6.2	32[c]	20[c]	[b]	30[c]
- low (% FS)	[a]	8.0	17[c]	40[c]	[b]	47
Field Response Time, 90%/95% FS (sec)	≤900	230/230	304/328	480/583	[b]	[b]
Instrument Operational Time[d] (%)	[a]	89	97	76	0	0

[a] Not specified.

[b] Data not complete due to instrument malfunction.

[c] Result of one test only.

[d] Time the instrument was producing useable data during 11-month field evaluation without considering the absolute accuracy of the data, i.e., without correcting for days the monitor was out of calibration. However, if the monitor was known to be malfunctioning and not just out of calibration, the monitor was condidered to be off line.

TABLE 10. SUMMARY OF H_2S RELATIVE ACCURACY TESTS AT REFINERY

TEST NO.	START DATE	NUMBER OF REFERENCE METHOD SAMPLES	METHOD 11 MEAN H_2S CONC (ppm)	RELATIVE ACCURACY							
				BENDIX		HOUSTON ATLAS		DEL MAR		TELEDYNE	
				% std[a]	% [H_2S][a]	% std[a]	% [H_2S][a]	% std[a]	% [H_2S][a]	% std[a]	% [H_2S][a]
1	4/27/80	9	159	28.9	29.9	b	b	25.1	25.9	115	119
2	5/5/80	9	201	39	32	b	b	52.4	43.0	74	61
3	6/9/81	9	208	58.8	47.4	47.1	37.9	45.8	36.3	b	b
4A	1/20/81	9	190	18.5	16.1	13.8	12.0	28.4	24.7	b	b
4B	1/20/81	9	197	16.4	13.7	30.0	25.1	48.9	40.9	b	b
5	2/18/81										
	Lab 1	9	34.6	18.1	86.4	24.4	116	32.0	153	b	b
	Lab 2	7	31.7	22.4	117	28.9	148	39.4	205	b	b
6	2/25/81[d]	6	150	11.1	12.2	c	c	c	c	b	b
7	2/25/81	8	138	33.5	40.2	c	c	c	c	b	b
8	3/31/81[d]	10	114	8.3	12.0	b	b	21.5	31.1	b	b

[a] Standard = 165 ppm H_2S. Span [H_2S] = Method 11 result.

[b] Monitor not operational.

[c] Monitor operational but not included in test because it could not be brought into calibration.

[d] Fuel gas spiked with known amount of H_2S using Houston Atlas, Inc. Model 601 diluter.

TABLE 11. CALIBRATION DRIFT TEST RESULTS FOR H_2S MONITORS

TEST NUMBER	CALIBRATION DRIFT[a, b] (%)					
	BENDIX		HOUSTON ATLAS		DEL MAR	
	Zero	Span	Zero	Span	Zero	Span
Test 1						
1	0	0.7	0.1	6.3	12.5	21.3
2	0	0.7	0.3	4.5	9.6	30.9
3	0	1.1	0.4	0.3	19.5	52.6
4	0	1.1	0.1	1.0	0.7	101
5	0.1	9.2	0.3	13.9	4.8	44.0
6	0.1	8.1	0.1	13.9	0	3.3
7	0	0.7	6.9	2.9	2.6	8.1
Test 2						
1	0	1.1	3.5	10.8	6.6	34.2
2	0	0	1.4	26.0	4.4	26.5
3	0	0.7	4.5	3.5	1.5	2.6
4	0.2	0.4	4.2	3.1	1.5	2.6
5	0.1	2.6	1.0	12.8	1.5	1.8
6	1.0	1.1	0.6	1.4	0	0
7	0.1	0.4	-	11.5	4.0	4.8
Test 3						
1	0.1	1.8	0.1	4.9	1.1	7.4
2	1.0	0.7	0.3	1.0	0.4	6.6
3	0.2	0.7	1.7	15.6	1.1	8.5
4	0.2	1.5	5.2	21.5	10.7	6.6
5	0.1	1.5	7.6	-	9.9	18.4
6	4.2	2.9	5.9	4.9	0	6.3
7	4.2	4.0	2.1	5.2	1.5	3.7
Test 4						
1	0	0.7	3.1	3.8	0.4	1.1
2	0	0	0.7	6.6	0.7	3.7
3	0	0.7	0.7	0.7	0	0
4	0	0	0	0.7	0.6	4.8
5	0	0	0	6.6	2.0	12.1
6	0	0.4	0	0	-	-
7	-	-	0.3	10.4		

[a] Values in table represent the daily drift as defined by the following equation

$$\frac{|\text{Calibration Gas Concentration} - \text{Monitor Reading}|}{\text{Monitor Span Value}} \times 100\%$$

[b] Because long-term drift was of primary concern, the instruments were not zeroed daily. The values in the table have been corrected by the daily zero drift.

SECTION 3

RECOMMENDATIONS

CARBON MONOXIDE CONTINUOUS EMISSION MONITORS

The Anarad and MSA monitors successfully completed the 11-month study and demonstrated that monitors with good drift control are available and suitable for the measurement of CO concentrations in FCC emission gas. Based on the results of this study, the following specifications are advanced for CO monitors.

- Calibration Drift. The CEMs calibration must not drift or deviate from the reference value of the calibration gas by more than 5 percent of the established span value of 1,000 ppm over each 24-hour operating period.

- Relative accuracy (RA). The RA of the CEMs must be no greater than 20 percent of the mean value of the reference method (RM) test data in terms of the units of the emission standard or 15 percent of the applicable standard, whichever is greater, as calculated using Equation 2-4 in Reference 4 and the manual CO method results as the reference value.

The correlation among the reference method and CEM data, the number of RM tests and the calculations should be the same as those given in Section 7 of Performance Specification 2(4).

Because of the possibility of leaks when sampling with Tedlar bags, the number of samples taken for a relative accuracy test should be at least twelve with the option of discarding the results from any three if it appears that leakage has occurred. The relative accuracy testing should be done while the CO concentration in the emissions is varying less than 10 percent over the duration of the testing.

HYDROGEN SULFIDE CONTINUOUS EMISSION MONITORS

The performance of the H_2S monitors was disappointing. Only three of the five monitors were suitable for field use and only one monitor (Bendix) had an uptime in excess of 85 percent. The other two monitors that passed the test suffered severe drift problems. The Bendix

sampled a total of 17 times each hour, but each sample duration was less one second. Thus, the use of the integrated Method 11 sampling approach for determining the accuracy of this monitor is questionable unless the fuel gas H_2S concentration can be held constant. The absolute agreement between Method 11 and all the monitors was poor and variable in eight of the ten relative accuracy tests as shown in Table 10. Since the cause or causes of this difference could not be identified, the use of H_2S monitors for compliance purposes cannot be recommended at this time.

The monitors may be useful, however, for determining trends and for indicating amine treater performance, as shown by the overall agreement between the average for all Method 11 tests and that for each monitor (i.e., Method 11-140 ppm, Bendix-119 ppm, Houston Atlas-130 ppm and Del Mar-133 ppm). (Some Method 11 tests used in calculating the above averages were not reported in the text of this report because they represented cases where plant malfunction or instrument failure caused a relative accuracy test to be aborted before an adequate number of samples had been obtained).

Due to the apparent bias between the Reference Method 11 tests and the H_2S CEM data, an interference to the reference method tests is suspected. Additional evaluation of the reference method should be performed before performance specifications are developed and installation of monitors is required.

SECTION 4

DESCRIPTION OF EQUIPMENT

CONTINUOUS EMISSION MONITORS

Carbon Monoxide Monitors

Applied Automation Optichrom 102--

The Model 102 is a gas chromatograph that uses a flame ionization detector (FID) to detect methane catalytically produced from carbon monoxide. The oven, valves and controls are located in an air purged module and the programmer is in a separate cabinet. A sample loop is used to sample an exact volume of gas which is injected onto the column by a multiport valve. Two columns in series are used for the separation - when the CO has eluted through the first column, it is backflushed to remove the heavier components while additional separation takes place on the second column. A catalytic methanator converts the CO to methane (in the presence of hydrogen carrier gas) which is detected by the FID.

Automatic zeroing is accomplished via an auto zero control on the detector immediately before the CO peak reaches the detector. Spanning is accomplished by a series of attenuation switches and a fine attenuation potentiometer.

Ecolyzer 3107--

The Ecolyzer Model 3107 monitor utilizes an electrochemical sensor to measure CO in the ranges of 0 to 1000 ppm and 0 to 500 ppm. The unit utilizes a sampling pump and a by-pass to vent unused sample around the sensor. To maintain constant sample humidity, a salt water humidifer is located upstream of the detector. An absorbent cartridge is provided for the removal of SO_2 and NO_x from the sample gas. Sample pressure must not exceed 2.5 cm water at the sample pump inlet.

Mine Safety Appliances Lira 202--

The Lira 202 has two IR lamps, a "Luft-type" infrared detector and gold-lined sample and reference cells. One lamp passes through the sample cell and the other lamp through the reference cell. The emergent radiation from both cells is directed to a single detector cell. As the gas in the detector absorbs radiation, its temperature and pressure increase. An expansion of the gas in the detector causes the membrane of a condenser microphone to distort. This distortion is converted to an electrical signal which is amplified to produce an output signal. The entire analyzer is kept at a constant temperature by a thermostatically controlled heater and blower installed in the case.

Anarad 501R—

This NDIR analyzer uses unlined Plexiglass sample and reference cells. The monitor consists of a single IR source, parabolic mirrors, a chopper, an optical solid state detector and an output module that can be separated from the rest of the monitor.

Hydrogen Sulfide Monitors

Bendix 7770—

The Model 7770 gas chromatograph monitors H_2S using an FPD. A sample block is used to inject a volume of sample gas onto the first column. After the H_2S has eluted through the first column, the column is backflushed to remove the heavier components. Further separation is attained in the second column prior to H_2S detection. Zeroing is automatic during the running program, but a zero offset control is also provided inside the programmer. The instrument cycle time is 210 seconds. Clean, dry air is used as the carrier gas.

Process Analyzers Incorporated 32-230—

The Model 32-230 monitor is a gas chromatograph equipped with a flame photometric detector (FPD) that is sensitive to sulfur. A volume of sample is injected into the analytical column from a sample loop. After the H_2S sample has eluted past the first column, the column is backflushed to remove heavier compounds. The H_2S continues through the second column. At the proper time for the H_2S component to elude through the column, the flame photometric sensing circuit is activated to detect the H_2S. Zeroing is automatic and occurs immediately before the elution of the peak of interest. Span is accomplished by adjust- ing an attenuation potentiometer inside the case.

Teledyne 611 DMCO-20X—

This dual beam monitor utilizes ultraviolet absorption to quantify H_2S concentration in the sample. A 12-inch-long optical cell has continuous sample flow. On one end of the sample cell is an ultraviolet source and on the other end a detector. A rotating chopper with two filters 180° apart is located between the cell and the detector. One of the filters passes only a known absorption wavelength for H_2S, the other a wavelength at which H_2S does not absorb (reference beam). The wavelengths are not specified. Synchronizers and electric circuitry subtract the non-H_2S absorption (reference beam) from the total absorption.

Houston Atlas Model 825R/102—

The Model 825R/102 monitor operates on the principle of lead acetate impregnated paper tape reacting to change color in the presence of H_2S. A cadmium sulfide photocell is used as a detector. The photocell output feeds a preamplifier. The output of the preamplifier feeds a low-pass filter which differentiates the signal with respect to time. The resultant differentiated output provides a DC signal that has a peak amplitude directly proportional to the H_2S concentration.

To obtain a sample in the concentration range of measurement by lead acetate tape, the monitor is equipped with a sliding block diluter. This diluter mixes a measured volume of sample with a stream of diluent gas. The amount of dilution is adjusted by varying the injection frequency of the sample. Zero and span adjustments are made by adjusting potentiometers inside the case.

Del-Mar Scientific DM-W--

The DM-W uses a lead acetate impregnated paper tape that is exposed to the gas stream as it moves past an aperture. The H_2S in the gas stream causes a black precipitate (lead sulfide) to form on the tape. Color development is monitored by a photocell that measures light reflected off the tape.

Because the DM-W normally operates in the 0 to 50 ppm H_2S range, Del Mar supplied a dilution system with the monitor. This system was comprised of two rotameters, a mixing chamber and a back pressure regulator. The fuel gas sample was diluted with nitrogen at the recommended ratio of 1:10 by adjusting needle valves on the rotameters.

ANCILLARY EQUIPMENT

All monitors and data aquisition equipment were installed in a 24-foot-long trailer equipped with heating and air conditioning. Figure 2 shows the location of all equipment within the mobile laboratory.

The CO source was a stack on a FCC unit. The CO boiler stack gas contained: 150 to 300 ppm NO_x, 200 to 600 ppm SO_2, some acid mist, 50 to 300 mg/m^3 particulate matter, 10 to 14 percent H_2O, 9 to 14 percent CO_2, and 20 to 10,000 ppm CO. The temperature at the sampling point was approximately 320°C (600°F).

The H_2S source was a fuel gas pipeline located approximately 120 meters from the trailer. Stainless steel tubing (0.63 cm OD) was used to connect the gas line to the trailer H_2S distribution system. The sampling point was downsteam of an amine treater. When the monitors were first installed in April 1980, the treater was using diethanolamine for the removal of H_2S, but in March 1981, the treater was refurbished and monoethanolamine replaced the diethanolamine. The H_2S level in the fuel line ranged from 5 to over 1,000 ppm during this study.

Fluid Catalytic Cracker Emission Sampler/Conditioner

An EPA-designed sample conditioning system was located at the sampling port 60 meters above ground level on the CO boiler stack. The dried (dewpoint -20°C) and filtered sample was transported 200 meters to the trailer by using unheated, 9.5 mm ID black, nylon tubing. A detailed description of the sample conditioning system and its per- formance is included in Appendix D.

Sample Distribution Systems

In the trailer, the gas samples from the sources were distributed to the monitors by using the distribution (manifold) systems shown in Figures 3 and 4. The water column was included on the CO distribution system to ensure that constant pressure was maintained in the system. In addition, a pressure reducer was included to ensure that the Ecolyzer inlet pressure was maintained below 2.5 cm water. Each distribution systems was fitted with solenoid valves on the span gas and nitrogen gas lines to facilitate automatic daily zero and span checks by the data aquisition system.

Data Acquisition System/Automatic Zero/Span System

Each monitor was connected to the Esterline Angus Model PD-2064 data logger. The PD-2064 converted the 4 to 20 mA output of each monitor to 25 to 125 mV and provided approximately a -25 mV offset. Each instrument then showed a response on the PD-2064 of 0 to 100 mV. The PD-2064 is able to monitor all 16 channels continuously or to scan them at any desired frequency. In addition, the system can scan selected channels at any desired interval and average the readings for each channel after the desired number of scans. During the field testing, each monitor's output was scanned every 3 minutes except when relative accuracy and calibration error tests were conducted. In those cases scan times of 1 minute were usually used. After ten scans, the readings were averaged and the results were printed on the paper tape. The data and time of printing were also recorded on the tape.

Every 24 hr, the data logger automatically accomplished a zero/span check of the monitors. At a set time the data logger closed the contacts leading to a solenoid valve in the sample distribution system. This valve shut off the sample gas and opened the nitrogen (zero) gas. After 15 minutes the data logger took a single reading on each channel and printed the value. The first set of contacts then opened and a second set closed to allow span gas to enter. After 15 minutes the data logger again read each channel and printed the value. The second set of contacts then opened and the original program of scanning and printing resumed.

EPA Reference Method 11 was used throughout as published. Equipment listings are published in the Method.The manual method for CO analysis is presented in Appendix E. All equipment is described therein.

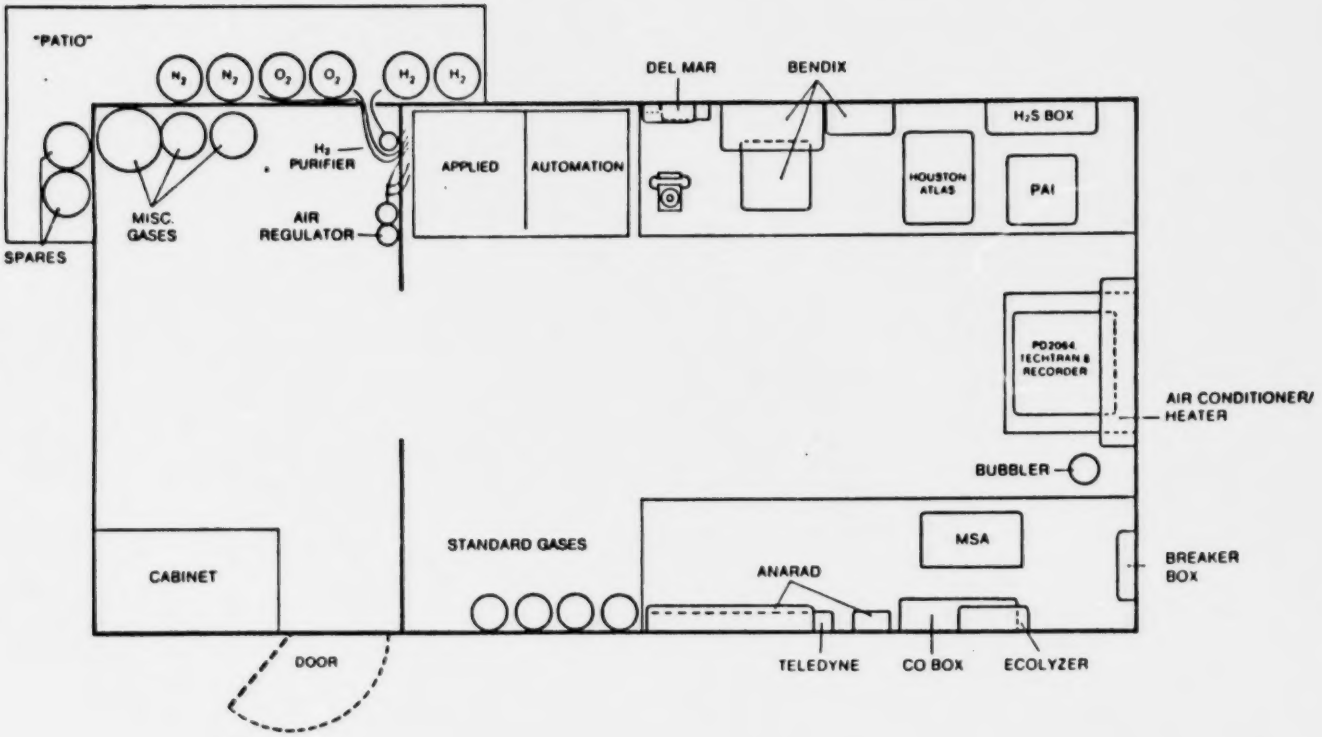

FIGURE 2. SKETCH OF INSTRUMENTATION TRAILER SHOWING INSTRUMENT ARRANGEMENT.

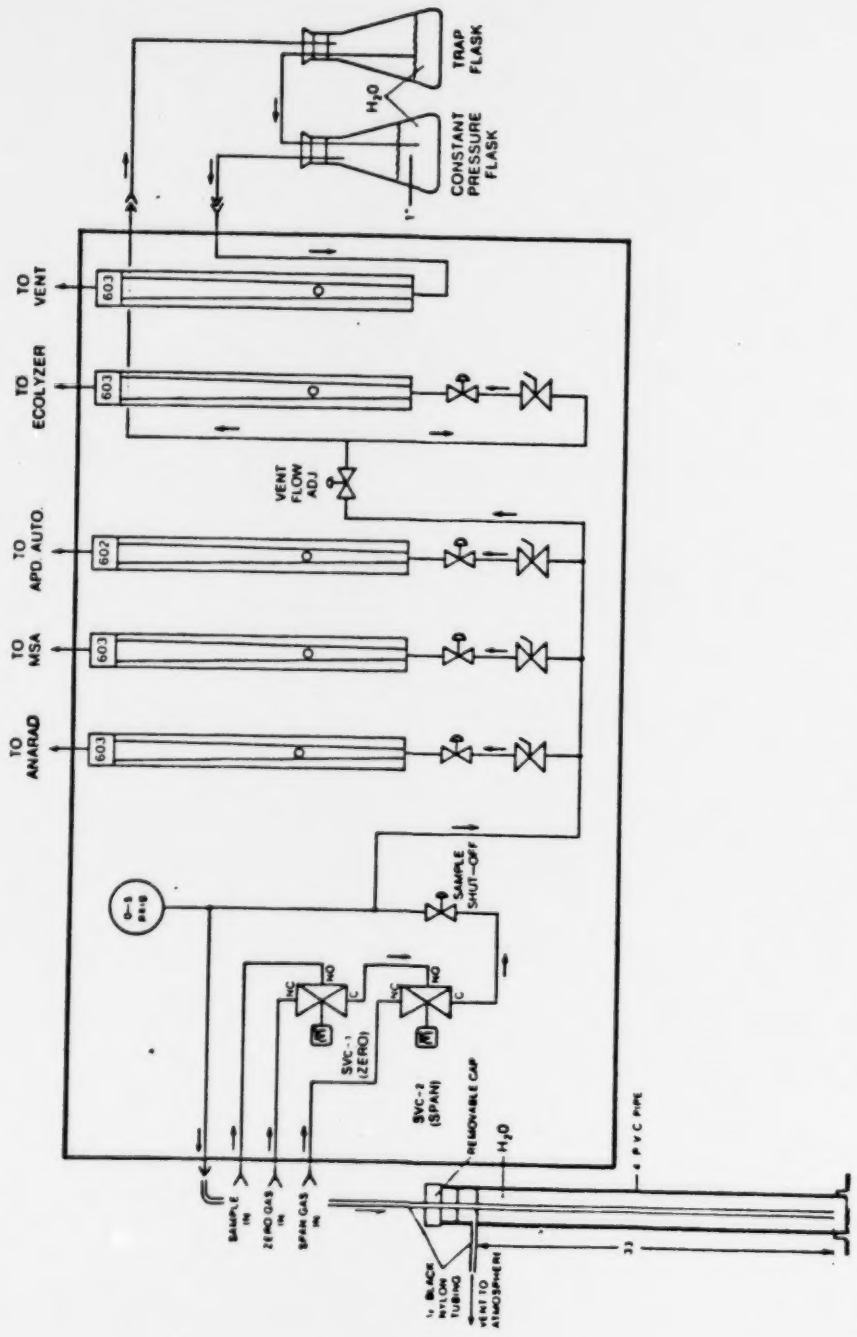

FIGURE 3. PLUMBING DIAGRAM FOR FCC GAS DISTRIBUTION TO THE CO CEMS

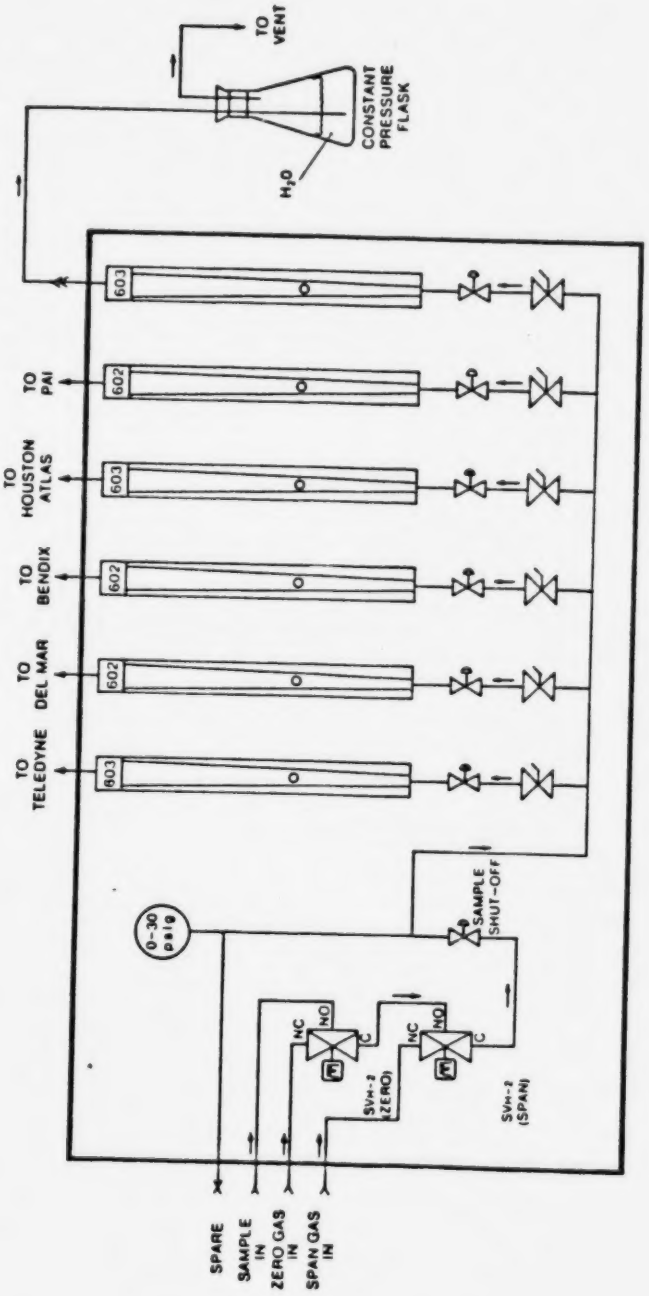

FIGURE 4. PLUMBING DIAGRAM FOR FUEL GAS DISTRIBUTION TO THE H_2S CEMS

SECTION 5

EXPERIMENTAL PROCEDURES

GENERAL PROCEDURES

Calibration Gases

Calibration gases used for this evaluation were Certified Master Gases supplied by Scott Specialty Gases, Plumsteadville, PA. Calibration gases were selected to be 15, 50, and 90 percent of the instruments' span range with nitrogen being the balance. The gases were analyzed and certified to be ±2 percent of the stated values. Method 11 was used to verify the H_2S gas concentrations and a Bendix Model 8501 5CA NDIR CO monitor calibrated with NBS standards, was used to verify the CO gas concentrations.

Calibration Procedures

Each instrument was calibrated according to the manufacturer's instructions by using the appropriate sample distribution system to introduce the calibration gas. Calibration curves were generated for each monitor.

Throughout this evaluation, all instrumental response readings were obtained from the digital millivolt output on the Esterline Angus PD-2064 data logger. Span and zero adjustments were made on the instruments to produce a proper millivolt response on the PD-2064 data logger.

LABORATORY EVALUATION OF THE MONITORS

The monitors were evaluated in the laboratory with the procedures described in the Federal Register(5). The following parameters which are defined in Appendix A, were evaluated:

- precision
- noise
- response times (rise and fall)
- H_2O and CO_2 interference for CO monitors
- CH_4 and CH_3SH interference for H_2S monitors
- flow and temperature variation

Precision (Repeatability)

Precision is the standard deviation about the mean of repeated measurements on the same gas concentration (2). In this test, measurement of the selected gas (e.g., mid-span) was interrupted alternately by the introduction of a higher and a lower gas concentration. Six stable readings of the selected gas were obtained in this manner and the precision was calculated as follows:

$$P = \sqrt{\frac{1}{5}\left[\sum_{i=1}^{6} P_i^2 - \frac{1}{6}\left(\sum_{i=1}^{6} P_i\right)^2\right]} \qquad (1)$$

Where: P = Precision
P_i = Instrument response (ppm) for the i^{th} measurement on the selected gas.

Output Noise

Instrument noise is a short-term variation in instrument output not caused by changes in output concentration. This value is expressed in concentration units as the standard deviation about the mean (2).

The test procedure involved allowing the instrument to stabilize on the gas standard (either zero or span) and then taking 25 readings within a 60 minute period by using a digital voltmeter. These readings (expressed in concentration units) were entered into the following equation:

$$S = \sqrt{\frac{1}{24}\left[\sum_{i=1}^{25} (r_i)^2 - \frac{1}{25}\left(\sum_{i=1}^{25} r_i\right)^2\right]} \qquad (2)$$

Where: S = Instrument Noise (ppm)
r_i = Instrument Response for the i^{th} reading (ppm)

Instrument Response Time

Rise time is the time interval between the initial instrument response and 95% of the final response after a step increase in input gas concentration. The test procedure involved changing the input from zero gas to a high-range span gas and determining the time required to reach 95% of the high-range span gas concentration.

Fall time is the time difference between the initial response and 95% of the final response after a step decrease in input gas concentration. The test procedure involved changing the input from a high-range span gas to zero gas and determining the time required to reach 5% of the span value.

To obtain the proper rise and fall times, the "dead volume" in the sample lines was minimized by placing a three-way stopcock as near as possible to each instrument's sample port. The sample gas was switched from zero to span by using this three-way stopcock. The chart recorder was used at its fastest speed during the test. The response times were calculated from the strip chart. Three rise times and three fall times were calculated and the results of each set were averaged. The instrument response reported in Tables 5 and 9 is the larger of these two values.

CO_2 and H_2O Interference for CO Monitors

Carbon dioxide interference was determined by using a Scott blend of 10 percent CO_2 in nitrogen. The response to the introduction of the 10 percent CO_2 is expressed in ppm as an equivalent CO concentration.

Water interference was determined by adding water vapor while the instrument was sampling nitrogen (zero gas). The response to the added water vapor was expressed in ppm as an equivalent CO concentration. Water vapor was added by passing nitrogen through a flask containing distilled water. The flask was heated sufficiently to introduce the desired amount of water vapor into the flowing gas without causing condensation in either the sample lines or the instrument. The water vapor generator was calibrated using EPA Method 4.

Methane and Methyl Mercaptan Interference for H_2S Monitors

Methane interference was determined using 99 percent methane. Each instrument was first zeroed and calibrated according to the manufacturer's instructions. The methane was then introduced and the response was recorded as ppm H_2S. This same procedure was repeated using 40 percent hydrogen in methane and 200 ppm methyl mercaptan in methane. The interference was expressed in ppm as an equivalent H_2S concentration.

Variations in Response Due to Changes in Temperature and Sample Flow Rate

Variations in instrument output caused by short-term changes in ambient temperature were measured using zero and span gases. The test procedure involved allowing the instrument to stabilize at a given room temperature, recording the response to a gas, changing the temperature $\pm 10^{\circ}C$ and again recording the stabilized response. This test was performed using the trailer's heating and air conditioning system to control the room temperature.

Variations due to flow rate changes were studied using rotameters calibrated with a soap-bubble flowmeter. The span gas and the flow rate were varied from approximately 20 to 500 percent of the recommended sample flow rate. The instrument response was plotted versus the percent of recommended flow.

FIELD EVALUATION OF THE MONITORS

Field Response Time

Field response time is the time required for the instrument to obtain either 90 or 95 percent of the final instrument response after a step increase in the gas concentration. In the study this included the time involved for gas flow through the sample conditioning system. The gas was introduced at the sampling point and the response time was calculated in a manner similar to that used in the laboratory evaluation of instrument response time.

2-Hr Drift (Zero and Span)

At 2-hr intervals, zero gas (nitrogen) was sampled by the monitors until all of the monitors had obtained a stable reading; then, the span gas was introduced to all of the monitors. The zero and span values were recorded by the data logger and the source gas was sampled again until the next 2-hour interval was to begin. At this time the above procedure was repeated. This was continued until fifteen 2-hour intervals were completed. Instrument zero and span were adjusted only at 24-hr intervals during this test, and none of these adjustments were made during the time a 2-hr interval measurement was being made. The 2-hr zero drift was calculated in the following manner:

$$\text{Drift (zero or span)} = \frac{[\,|\bar{d}| + CI\,] \times 100\%}{\text{Instrument Span}} \qquad (3)$$

where

$\bar{d} = \frac{1}{n} \sum_{i=1}^{n} d_i$ = Algebriac mean of the differences

d_i = (instrument reading) - (instrument reading 2 hours later)

n = Number of data points (i.e., the number of d_i values)

CI = 95% confidence interval estimate of the mean value

$$\frac{t_{0.975}}{n\sqrt{n-1}} \sqrt{n \sum_{i=1}^{n} d_i^2 - \left(\sum_{i=1}^{n} d_i \right)^2} \qquad (4)$$

$t_{0.975}$ = Student's t-factor, function of n; i.e.

n	$t_{0.975}$	n	$t_{0.975}$
2	12.706	8	2.365
3	4.303	9	2.306
4	3.182	10	2.262
5	2.776	11	2.228
6	2.571	12	2.201
7	2.447	14	2.160
		15	2.145

The 2-hr span drift was calculated in an analogous manner, except that the span reading was corrected for any zero drift that occurred in the 2-hr interval.

24-Hour Drift (Zero and Span)

The data logger automatically introduced zero and span gases into the sample distribution systems daily and the instrument response was automatically recorded by the data logger. Seven consecutive values were obtained over a one week period to establish the 24-hr drift for each monitor. Zero and span were adjusted only at 24-hr intervals on an as needed basis. Equations 3 and 4 were used to calculate the 24-hr zero and span drift values.

Calibration Error Test

The calibration error test was performed by first calibrating each instrument, then alternately introducing each calibration and zero gas until fifteen readings were obtained. The difference between the instrument's response and the actual concentration of each gas was then calculated using equations analogous to 3 and 4. (In Equation 3, the calibration gas concentration would be the denominator and not the span value of the instrument).

Calibration Drift

Data for this test were taken from the daily zero and span checks. Zero and span adjustments were made at weekly or longer intervals.

Relative Accuracy

The relative accuracy of the CO monitors was determined using the leuco crystal violet wet chemical method described in Appendix E. The accuracy of the H_2S monitors was determined using EPA Reference Method 11 (6). The relative accuracy of the monitors was calculated as described in Reference 4, i.e.:

$$\text{Relative Accuracy (\%)} = \frac{[|\bar{d}| + CI] \times 100\%}{\text{Mean Value of Reference Method}} \quad (5)$$

where

$\bar{d}$ = Algebraic mean of the difference between the reference method value and the monitor value

CI = 95% confidence interval

SECTION 6

RESULTS AND DISCUSSION

MANUAL CO METHOD DEVELOPMENT/VALIDATION

EPA Reference Method 10 specifies collecting the emission gas sample in a Tedlar bag and analyzing for CO by NDIR (7). Since NDIR is the measurement principle used in most CO CEMs, EPA desired to have a non-NDIR manual method for checking the accuracy of NDIR-equipped CEMs. Four wet chemical CO methods previously described in the literature (8-12) were evaluated in this study.

The first method evaluated (8) involves the aqueous reduction of Pd(II) by CO followed by the addition of KI to yield a red, tetraiodo-palladium (II) complex, which is then measured spectrophotometrically to determine the amount of Pd(II) reduced. The amount of CO present in the gas sample is then calculated on the basis that two moles of CO reduce one mole of Pd(II). Although this method performed adequately in the laboratory, it was found unsuitable for gas samples that contained even 1 ppm NO. For example, the following analytical results (ppm CO) were obtained on three Tedlar bag samples that contained 266 ppm CO and the following levels of NO in nitrogen: 225 ppm NO (27 ppm); 2 ppm NO (186 ppm); and 1 ppm NO (223 ppm). The method suffered from: interference by SO_2 and organics; sample instability; poor precision below 100 ppm CO and had a nonlinear absorption curve. Because of the slowness of the reduction of Pd(II) ion by CO, the method also required shaking the sample bulb for 2-hr before adding the KI. For these reasons, work on this method was terminated.

Three other methods were then evaluated. These methods used spectrophotometry and the reduction of Pd(II) ion by CO in the presence of gum arabic (9), phosphomolybdic acid/acetone (10) and leuco crystal violet/potassium iodate (11, 12). The gum arabic method suffered from poor precision, sample instability, and interference from low levels of NO and SO_2 and required a long reaction time (2 hr minimum). The molybdenum blue reaction also suffered sample stability problems, had poor precision for CO concentrations near the level of the standard (500 ppm) and required a sample reaction time of 1 hr at 60°C $\pm$ 1°C. Further, in both the gum arabic and phosphomolybdic methods, the reaction product is a colloid, which means that a strongly absorbing solution cannot be diluted to bring it into the linear range of the calibration curve.

The last method evaluated, the leuco crystal violet (LCV) method, yields a soluble complex that permits sample dilution, has good precision in the range of 0 to 1000 ppm, and is accurate in the presence of low levels of SO_2 and NO (<5 ppm). Some other favorable features are:

- the shaking reaction time can be as short as 15 to 20 minutes for CO concentrations from 50 to 1,000 ppm;
- the absorbance increases linearly with increased shaking reaction time up to 2 hours;
- the stock reagents are stable and easily prepared;
- the calibration curve is linear in the absorbance range 0 to 1.7;
- the complex that is formed absorbs in the visible region of the spectrum (587 nm) more than 200 nm from where the reagents absorb. Also, the blank is initially negligible (Table 12).

Since the LCV method suffers interference from SO_2 and NO at the concentrations encountered in FCC stack gases (Table 13), the effectiveness of various scrubbing solutions in reducing these compounds to less than 5 ppm (without also removing CO) was studied as a function of flow rate, scrubber volume, concentration and pH, gas volume, and SO_2 and NO concentration. The following scrubbing solutions were evaluated: 6% percent H_2O_2; 2 percent $KMnO_4$/2 percent NaOH; 4 percent $KMnO_4$/4 percent NaOH; 2.5 percent $KMnO_4$/1 percent HNO_3; and 2 percent $K_2Cr_2O_7$/1 percent HNO_3.

The best scrubbing system is a flow rate of 0.2 to 0.3 L/min through three Greenburg-Smith impingers. The first two impingers contain 400 mL of 4 percent $KMnO_4$/5 percent NaOH and the third 250 mL of this solution. This system can reduce the SO_2 and NO levels to less than 5 ppm for a 50-liter gas sample containing 15% CO_2, 700 ppm SO_2 and 500 ppm NO. Since the impinger system also removes CO_2, an appropriate volume correction is required when calculating the CO concentration originally present in the gas. A Fyrite analyzer is suitable for measuring the CO_2 present in the stack gas.

For field sampling, the original single-sample, ambient air method (12) was modified to allow the analysis of many samples in a short period of time under field conditions. Sample stability, shaking time, shaker type, sample volume, and volume of reagent were

some of the parameters studied to simplify the method as much as possible and at the same time to optimize its precision and accuracy at stack CO concentrations.

The method was validated at the petroleum refinery in four field tests in which the samples were passed through the scrubber solution and collected in 10-liter Tedlar bags. These bag samples were returned to the laboratory and analyzed in triplicate by the LCV method and by NDIR on a Bendix Model 8501-5CA calibrated against NBS certified CO standards. From forty-one samples collected and analyzed in this manner, it was determined that the manual method had a consistent 4 percent positive bias with respect to the NDIR. The precision of the method was determined to be 2.5 percent of the mean concentration for a sample that contained between 15 and 1000 ppm CO when the sample was analyzed in triplicate. The Tedlar bag samples were stable for at least two weeks. Representative analytical results are presented in Table 14 and the actual method is described in Appendix E.

Since the largest source of error was found to be leaks around the valve of the Tedlar bags, all bags should be checked for leaks before use, either by submerging filled bags in water or by pulling a vacuum (25 cm H_2O) on the bag and seeing if it will hold the vacuum for at least 4 hours.

TABLE 12. CHANGE IN ABSORBANCE OF CO REAGENT BLANK WITH TIME AT ROOM TEMPERATURE

TIME SINCE PREPARATION (min)	ABSORBANCE	
	THIS STUDY	REFERENCE 11
0	0.015	0.020
20	0.015	—
30	—	0.040
45	0.020	—
60	0.030	—
100	0.050	—
120	—	0.07
180	—	0.12
230	0.080	—
280	0.085	—
320	0.089	—
360	0.100	0.21

TABLE 13. EFFECT OF NO AND SO_2 ON LUECO CRYSTAL VIOLET

SAMPLE NUMBER	SO_2 (ppm)	NO (ppm)	CO (ppm)	
			ACTUAL	FOUND
1	0	200	500	410
2	0	400	500	290
3	700	0	500	290
4	500	200	500	360

TABLE 14. COMPARISON BETWEEN LCV AND NDIR RESULTS ON FCC SAMPLES

TEST DATE	LCV METHOD RESULTS (ppm CO) 1	2	3	AV	NDIR (ppm CO) BENDIX 8501-5CA
SEPTEMBER 1980	178	159	163	167	149
	121	120	129	123	115
	31.1	31.0	30.1	31.0	34.0
	78.6	91.1	76.4	82.0	75.0
	26.5	28.0	27.8	27.0	26.0
	25.2	24.0	26.9	25.0	22.0
	28.8	28.0	29.3	29.0	27.0
	16.7	17.6	16.5	17.0	19.0
	33.0	30.2	33.2	32.0	28.0
JANUARY 1981	1094	1002	1111	1069	1005
	356	365	321	347	315
	546	592	---	569	575
	176	184	182	180	178
	181	184	211	192	175
	158	145	153	152	155
	188	182	189	186	181
	81	87	78	82	62
	102	114	110	109	98
	519	482	536	512	539
	258	248	267	258	235

EVALUATION OF CARBON MONOXIDE MONITORS

Five relative accuracy tests were conducted on the CO monitors at the refinery. The results of these tests are summarized in Table 6 and the results of each run are presented in Table 15. In these tests, the samples for the manual method were passed through Greenburg-Smith impingers containing alkaline $KMnO_4$ solution (to remove NO_x, SO_x and organics) and then collected in Tedlar bags. All samples were collected from the distribution manifold to ensure that a sample-conditioning system malfunction did not contribute significant error to the monitor validation procedure.

Tests to verify that CO was not lost in the sample conditioning system were conducted before each relative accuracy test and at other times between February 1980 and April 1981. Until September 1980, these checks consisted of simultaneously collecting stack gas samples in Tedlar bags at the manifold (distribution box) and at the probe, and analyzing the bags by NDIR for CO and CO_2 at the EPA laboratory in Research Triangle Park, North Carolina. In September 1980, a Bendix Model 8501-5CA NDIR CO_2 analyzer was installed in the trailer to continuously measure the CO_2 concentration in the gas leaving the manifold. After this, the sample conditioning/sample transport system was checked monthly and also before each relative accuracy test by analyzing the stack gas for CO_2 using a Fyrite analyzer and by comparing the result to the Bendix 8501-5CA monitor reading. If the Bendix CO_2 monitor value differed by more than 0.5 percent from the Fyrite value, remedial action was taken before the relative accuracy test was initiated.

The operation of the FCC unit during this 11-month study was erratic due to FCC failure and process upsets. The CO levels varied between 20 ppm and 10,000 ppm CO over a period of several days; frequently, the particulate emissions were much higher than the 50 to 100 mg/m^3 normally present. Each time a relative accuracy test was conducted, the CO concentration in the stack exceeded the 1,000 ppm span range of the monitors, so plant instrument air was introducted at the probe to bring the CO concentration into the operating range of the monitors. This dilution also reduced the NO_x and SO_2 concentrations in the sample gas by factors of 4 to 10.

During each relative accuracy test, a cylinder gas containing 100 ppm CO, 12 percent CO_2, 500 ppm SO_2, and 200 ppm NO in N_2 was introducted at the manifold for 30 min and the monitors' output was recorded while the Tedlar bag sample was taken for analysis by the manual method. This served three purposes. First, it showed how the monitors would perform when sampling a stack gas representative of FCC exhaust gases. (Recall, it was necessary to dilute the stack gas with air to bring the CO level into the range of the monitors.) Second, it served as a control sample to establish how constant a monitor's response was to the same sample over the length of the study. Third, it provided a sample of known CO concentration so that the accuracy of the manual method (sampling and analysis) could be established.

During each of the 30-minute relative accuracy tests, the monitor output was read at 1-minute intervals. The first test, conducted in June 1980, was unsatisfactory because the manual method being evaluated (palladium/potassium iodide) suffered sample stability problems and interference from NO. Thus, the only way to evaluate monitor accuracy in this test (Table 15) is to compare one monitor to another (Runs 1-9) or to compare their response to the 100 ppm CO cylinder (Run 10).

However, since the other four relative accuracy tests were done using the LCV method, satisfactory manual method results were obtained. The fourth and fifth relative accuracy tests were performed during the same week. In the fourth test, three gas cylinders containing 500 ppm CO, 12 percent CO_2, and different levels of SO_2 and NO were employed to see how the monitors would perform if sampling an undiluted FCC stack gas. As expected, the Ecolyzer detector failed during the test from exposure to NO_x and SO_2 which were not effectively removed by the Model 2949 scrubber. In the first three relative accuracy tests, the Anarad and MSA monitors were quite stable, but, by the last two tests, they somtimes drifted up to 5 percent of span over several hours, but at other times remained stable for a day. This drift sometimes occurred only in the span and at other times only in the zero setting. No explanation is available for the difficulty.

As mentioned earlier, the only problem encountered with the LCV manual method was the tendency of the Tedlar bag to leak at the point where the valve enters the bag. This was a significant problem only in the fourth relative accuracy test where new sample bags were used and a small leak was found at the metal washer that served as a gasket between the valve body and the bag. This leak only occurred when the sample was withdrawn from the bag and for this reason was not detected when the bags were leak-checked by inflating them before use.

Two calibration error tests were performed: the first in May 1980 and the other in June 1980. The results are presented in Table 5. The interference of CO_2 on the monitors remained constant throughout the study.

Figures 5 through 10 show the long-term zero and span drifts in the CO monitors. These data, which were collected from May 1980 to January 1981, were used to determine the calibration drift of the instruments. (Recall that: (1) only the Applied Automation had automatic zero and that none of the instruments had automatic span correction; (2) the zero and span of the monitors were checked every 24 hours; and (3) except when relative accuracy tests were being conducted, the zero and span of the monitors were never adjusted at intervals shorter than 1 week.)

Applied Automation Optichrom Model 102

The instrument is comprised of two modules, a programmer and a GC-oven assembly. It was purchased without vendor installation and interconnecting wiring was not furnished. The instruction manual was furnished three weeks after the instrument was received; hence, the monitor was not operational as received. Extensive time was required to complete the instrument wiring and install the circuit boards. After the monitor was wired and installed, numerous startup problems were encountered. After a serviceman was sent by Applied Automation, it was determined that wire of too small a gauge had been used for the interconnecting wiring. Numerous other difficulties were encountered in obtaining the correct output signal.

To adjust the span, a lengthy procedure requiring a strip chart recorder and many adjustments is necessary. After the initial span adjustment, a trial-and-error method is used for fine tuning, although it is not specified in the instruction manual.

The response time is limited by the cycle time of the analytical program. The GC completes a cycle every 105 seconds. Varying the flow or pressure causes no response variance because a sampling loop vented at atmospheric pressure is used. An oven maintains a constant temperature for the chromatographic columns. Since the sample value is ambient temperature or in a thermostatically controlled area, it was not affected by changes in ambient temperature or sample gas flow rate.

In June 1980, a negative concentration was sometimes measured by the instrument. After careful examination of the chromatogram, this problem was related to a negative signal dip that occurred immediately before the CO peak eluted. Several trips to the refinery were made by HE&T personnel to repair the instrument with no success. In November 1980, Applied Automation performed a service call. After two days of work, the serviceman still could not correct the problem and further testing of this instrument was discontinued.

Ecolyzer 3107

This instrument performed without failure during the laboratory testing. Special provisions were necessary to ensure that a sample pressure of no more than 2.5 cm water pressure was present at the sample inlet port. The span and zero adjustments were not responsive and thus a slow drift in zero and span followed any adjustment in these controls.

Sample flow variations from 0.5 to 1.5 times the recommended rate caused response variations of 10 percent reduction and 3 percent increase, respectively. In varying the ambient temperature from 10°C to 30°C no change in response was observed.

For removal of NO_x and SO_2 from the sample stream, a gas scrubber cartridge (filter Model 2949) was supplied. This was located inside the case and required removal of the sensor for replacement. Because of the extremely short lifetime of these filters and the difficulty in replacement, the filters were relocated outside of the case during the field evaluation. Normal life expectancy of these filters in a stack gas containing 500 ppm SO_2 and 300 ppm NO_x is 1 to 5 days. These filters cost approximately $45 (a considerable operating expense). Filter failure caused damage to the electrochemical sensor (requiring replacement at considerable cost).

MSA Lira 202

The MSA Lira 202 operated as received. After less than a week of operation, the power supply and output signal circuit boards failed. After the boards were replaced, satisfactory output in the range of 4 to 20 mA could not be obtained, despite several replacements of each of these circuit boards.

In June 1980, an MSA serviceman corrected the problem. Instead of using the 4 to 20 mA output on the instrument, he used an isolated external converter to convert the normal 0 to 100 mV output to 4-20 mA. After this repair, the monitor operated well throughout the evaluation. Occasional optical realignment was required to maintain calibration. Excessive drift was sometimes observed.

Tests for response variation due to sample flow rate and ambient temperature changes were not peformed due to the late arrival of the instrument.

Anarad 501R

This NDIR monitor performed without any difficulty during the evaluation. No special provisions were necessary for the sample gas except that there had to be free discharge from the sample exit port. Sample flow variation from 0.3 to 5 times the recommended rate caused response variations of less than 1 percent. Varying the ambient temperature from 10°C to 30°C did not affect the response. Carbon dioxide and water did give a slight positive interferences. Overall, the instrument proved to be extremely accurate and reliable.

TABLE 15. RELATIVE ACCURACY TEST RESULTS ON CO MONITORS

TEST AND DATE	CO_2 Conc. (%)	CO CONCENTRATION (ppm CO)[a] LCV	ECOLYZER	ANARAD	*EA
RA Test 1 (June 80)					
1	3	b	189	199	173
2	3	b	198	211	185
3	3	b	198	209	174
4	3	b	299	319	292
5	3	b	413	441	417
6	3	b	376	376	367
7	3	b	396	394	370
8	3	b	376	375	340
9	3	b	311	321	339
10	12	b	165	113	105
RA Test 2 (Sept. 80)					
1[d]	2	167	117	150	136
2[e]	2	123	99	141	128
3[d]	2	82	85	80	73
4[e]	2	25	32	37	33
5[d]	2	29	40	44	43
6[e]	2	32	38	46	43
7[f]	12	104	142	101	100
Mean	—	80	79	86	79
RA Test 3 (Jan. 81)					
1[g]	1	1069	1030	1074	1095
2[f]	3	569	572	605	598
3[g]	1	181	185	194	173
4[g]	1	192	216	226	205
5[f]	12	107	206	104	95
6[g]	1	186	194	201	195
7[f]	3	527	608	634	639
Mean	—	404	430	434	428
RA Test 4 (Feb. 81)					
1[g]	12	537	1679	506	497
2[g]	12	513	1680	507	497
3[g]	12	507	1680	509	519
4[h]	12	479	1100	498	518
5[h]	12	537	1536	501	510
6[h]	12	497	1648	506	509
7[i]	12	501	1684	541	503
8[i]	12	465	1686	538	501
9[i]	12	525	1624	519	507
Mean	—	507	1591	514	507
RA Test 5 (Feb. 81)					
1[f]	3	713	j	755	715
2[f]	3	743	j	745	723
3[f]	3	701	j	749	719
4[f]	3	840	j	755	709
5[f]	3	694	j	782	731
6[f]	3	732	j	769	772
7[f]	3	769	j	750	753
8[f]	3	693	j	736	773
9[f]	3	701	j	726	728
Mean	—	712	j	750	736

[a] Results corrected for CO_2 interference.

[b] LCV method test was not used.

[c] Cylinder gas used: 100 ppm CO; 500 ppm SO_2; 200 ppm NO; balance N_2.

[d] Stack gas dilution 1:6 with instrument air.

[e] Stack gas dilution 1:10 with instrument air.

[f] Stack gas dilution 1:4 with instrument air.

[g] Cylinder gas used: 500 ppm CO; 400 ppm NO; 12% CO_2; balance N_2.

[h] Cylinder gas used: 500 ppm CO; 700 ppm SO_2; 12% CO_2; balance N_2.

[i] Cylinder gas used: 500 ppm CO; 200 ppm NO; 400 ppm SO_2; 12% CO_2; balance N_2.

[j] Monitor could not be calibrated. 905 ppm CO standard read 760 ppm.

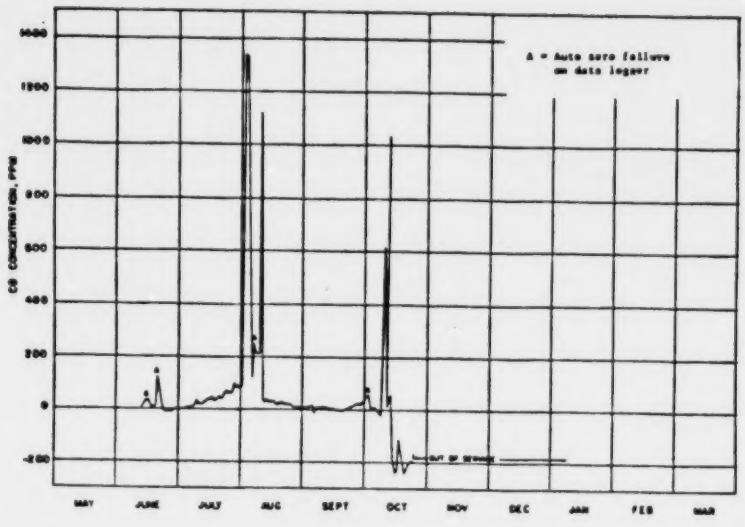

FIGURE 5. ZERO DRIFT TREND FOR ECOLYZER CEM.

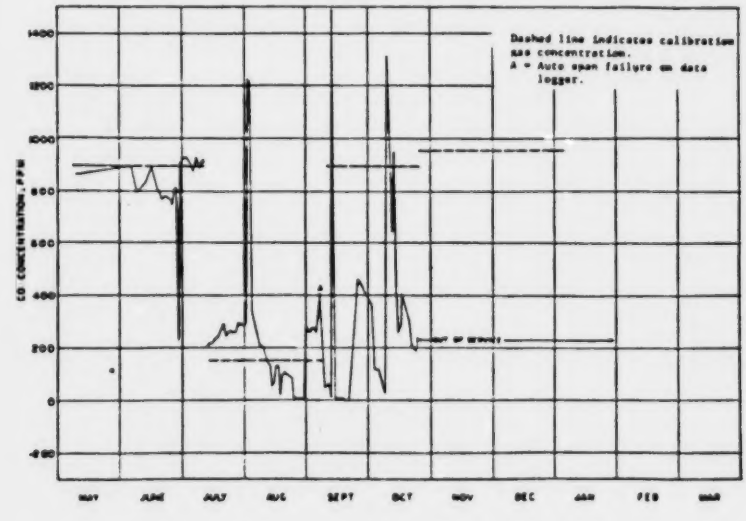

FIGURE 6. SPAN DRIFT TREND FOR ECOLYZER CEM.

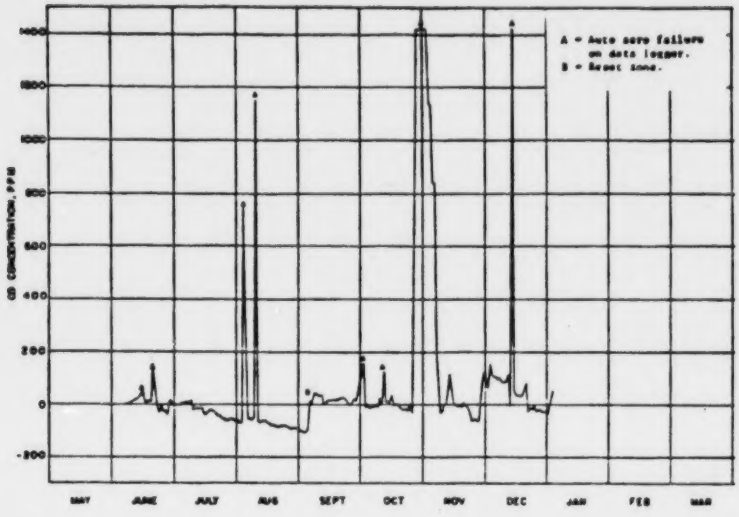

FIGURE 7. ZERO DRIFT TREND FOR MSA CEM.

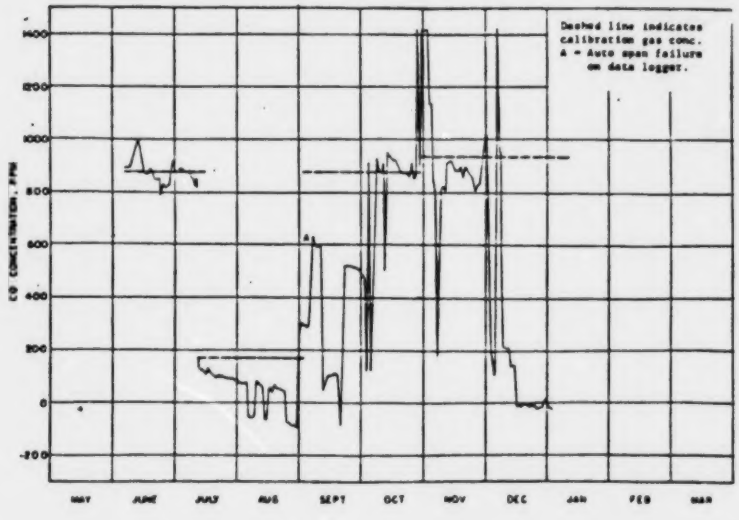

FIGURE 8. SPAN DRIFT TREND FOR MSA CEM.

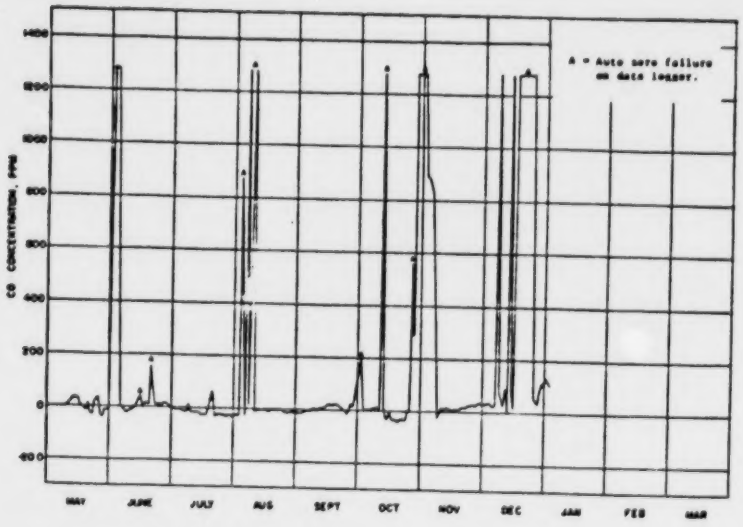

FIGURE 9. ZERO DRIFT TREND FOR ANARAD CEM.

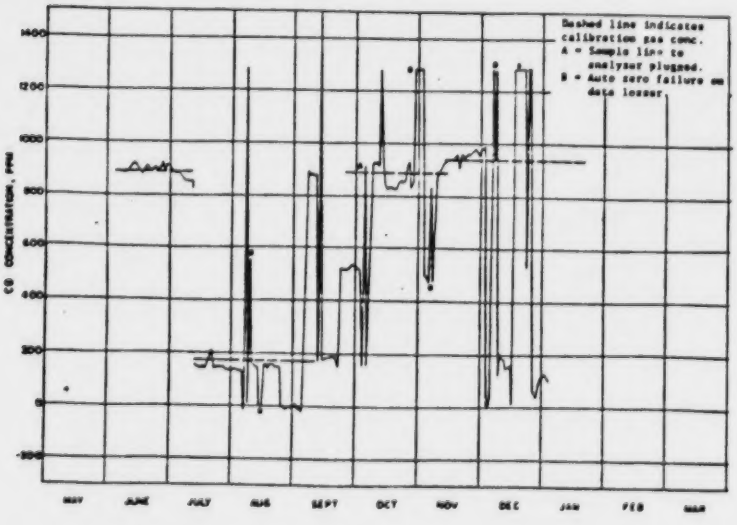

FIGURE 10. SPAN DRIFT TREND FOR ANARAD CEM.

EVALUATION OF HYDROGEN SULFIDE MONITORS

The results of the nine relative accuracy tests are summarized in Table 10. The individual test results are presented in Tables 16 and 17. From an examination of the data, the following observations are made:

1. When two laboratories simultaneously conducted a relative accuracy test of the monitors, very good agreement was obtained between the laboratories, but their results differed significantly from the monitors' results (Table 17, RA Test 5).

2. A monitor could compare well one day but poorly the next (Table 16, RA Test 4A, 4B). The overall agreement between Method 11 and the monitors, as measured by the relative accuracy tests, was quite variable over the length of the study (Table 16). This variability was also noted in the previous short-term study (3).

3. Generally, the Bendix and Houston Atlas monitors measured H_2S concentrations lower than Method 11, but on one occasion (RA Test 6, Table 16) the Bendix measured H_2S levels higher than Method 11. Experiments to determine the cause of these differences were inconclusive. When the fuel gas was spiked with known amounts of H_2S upstream of the manifold, the spike was adequately recovered by both the monitor (Bendix) and the Method 11 procedure. During these tests, (February and March 1981) the Houston Atlas monitor was not operational and the Del Mar was drifting severely, so only the Bendix results were reliable. The two laboratory collaborative test (Table 17) shows that the difference in concentrations was not due to laboratory bias in Method 11. Both Method 11 and the monitors agreed well when analyzing H_2S in nitrogen cylinder gases.

4. When the eighteen, 30-minute tests (Table 16, RA Test 4A and 4B) were grouped to yield nine 1-hour tests, the relative accuracy of the monitors with respect to Method 11 did not improve significantly. This indicates that increasing the sampling time to 1 hr does not significantly improve the results obtained.

Figures 11 through 16 show the long-term zero and span drift observed in the H_2S monitors. These data, which were collected from May 1980 to January 1981, were used to determine the calibration drift of the instruments. (Recall that: (1) only the Bendix and PAI had automatic zero and that none of the instruments had automatic span

correction; (2) the zero and span of the monitors was checked every 24 hr; and (3) except when relative accuracy tests were being done, the zero and span of the monitors were never adjusted at intervals shorter than one week).

Bendix 7770

This instrument is equipped with numerous safety devices including automatic shutdown and start up if certain hazardous conditions exist in the analyzer. A molecular sieve was added to the carrier air and hydrogen supply to ensure contamination free gases. The Bendix operated 89 percent of the time during field evaluation. Most of the downtime was attributable to two pneumatic valve failures; the downtime was lengthened due to personnel not being on-site to replace the part.

The flow variation and ambient temperature change tests were not applicable to this instrument because it used a heated sampling block to inject a constant and known volume of sample into the chromotagraph column, regardless of the sample flow rate. The cycle time of the instrument was 210 sec. For this reason, the time from injection to 100 percent response was used in the laboratory evaluation for response time rather than from first response to 95 percent of the final response.

The results of the precision, drift, noise and calibration error tests were excellent. Relative accuracy testing showed a consistant difference between the monitor and Method 11 for the fuel gas. The agreement was always good for H_2S in nitrogen. An interference in either the monitor or the reference method was indicated.

Process Analyzers Incorporated 32-230

This instrument never functioned properly. Many hours were spent troubleshooting circuit boards to attempt to find the cause for the lack of a proper output signal. The schematic wiring diagrams furnished in the operating and maintenance manual were not in agreement with the actual wiring. The unit was returned to the manufacturer for repair. After more than 4 weeks, it was returned to HE&T and installed in the test trailer on the final day of the first field evaluation. Before the next scheduled field evaluation, the monitor again failed due to a worn sample valve.

The output of the monitor was not the 4 to 20 mA specified in the equipment order; and thus the monitor was not compatible with the data aquisition system. Thus, its output was recorded on the narrow recorder supplied with the monitor. After several breakdowns, the monitor was shut off and its evaluation was discontinued.

Teledyne 611 DMCO-20X

This instrument required alignment of the chopper by using an oscilloscope prior to operation. Severe instability caused by any movement or vibration necessitated that laboratory testing be done at night when wind or personnel would not cause movement of the evaluation trailer. Significant interferences were caused by methyl mercaptan and other compounds found in fuel gas. The molecular sieve scrubber provided with the instrument could not correct the interference. An alternate scrubber was eventually furnished but complete failure of the instrument had already occurred. Because of multiple factors preventing acceptable operation of this monitor testing was discontinued before a valid test was achieved (See Appendix F).

Houston Atlas 825R/102

The instrument performed properly as received. The instrument's gas dilution system was not affected by sample flow rate or pressure changes, but it was affected by ambient temperature changes. That is, increasing the ambient temperature decreased the response in accordance with the ideal gas law. This affected the accuracy of the dilution.

Because of a wiring defect, the instrument did not operate during the first field test and was returned to the manufacturer. It was rapidly repaired and returned to the refinery.

Extremely large variance in the daily span values (10 to 30 percent) during the first 8 months of operation resulted from water condensation in the sample vent line. Increasing the downward slope of the vent line eliminated the problem.

The pneumatic actuator for the dilution system failed twice during the field evaluation causing monitor downtime. No specific interferences were detected but the general agreement between Method 11 and the monitor was not within the desired 10-percent range. Each time the lead acetate tape was changed, the monitor required recalibration. This required a minimum of 2 hr due to the instrument's slow response to calibration adjustment. A roll of tape lasted approximately 14 days.

Del Mar Scientific DM-W

The instrument operated as recieved, but before continuous operation was possible, the tension on the tape take up reel belt had to be increased by shortening the belt. The gas dilution system supplied by the vendor was inadequate. It was comprised of two rotameters (one for sample and one for dilution gas), a mixing chamber and a back pressure regulator. Slight changes in sample gas viscosity and

changes in both sample and dilution gas flow rate and pressure caused drastic calibration shifts in the instrument. Large volumes of dilution gas (10 L/min) were specified by the manufacturer. At this rate, a cylinder of nitrogen would last 1 day. Thus, to conserve gas, both sample and dilution flows were reduced to 15 percent of the recommended rate. Adverse effects were not noted by this reduction in flow.

Variations in sample pressure greater than 1 psi caused large variances in the sample flow to the dilution system, which in turn caused poor results in precision, noise and drift evaluations. The major problem with the instrument appeared to be the sample gas dilution system.

TABLE 16. RELATIVE ACCURACY TEST RESULTS ON H_2S MONITORS

TEST AND DATE	METHOD 11 RESULTS (ppm H_2S)	DIFFERENCE (Method 11-Monitor) (ppm H_2S) BE[illegible]X (ppm)	HOUSTON ATLAS (ppm)	DEL MAR (ppm)
RA Test 1 (4/27/80)				
1	161	43	37	-197
2	119	52	25	-248
3	165	47	4	- 77
4	172	21	37	-141
5	166	22	39	-138
6	167	32	40	-138
7	166	44	28	-147
8	158	38	34	-158
9	163	51	45	-153
Mean	160	39	32	-155
RA Test 2 (5/3/80)				
1	157	22	-6	-143
2	189	52	23	-104
3	173	50	25	-120
4	222	44	18	- 67
5	219	29	128	- 69
6	226	35	43	- 64
7	251	75	86	- 35
8	247	88	117	- 43
9	130	26	1	-158
Mean	202	47	48	- 89
RA Test 3 (6/9/80)				
1	262	99	76	80
2	269	96	67	87
3	226	73	50	49
4	245	91	74	68
5	199	78	61	86
6	233	102	86	33
7	219	82	78	30
8	163	62	47	37
9[a]	28	28	28	28
Mean	205	79	63	55

(Continued)

TABLE 16. RELATIVE ACCURACY TEST RESULTS ON H_2S MONITORS

TEST AND DATE	METHOD 11 RESULTS (ppm H_2S)	DIFFERENCE (Method 11-Monitor) (ppm H_2S)		
		BENDIX (ppm)	HOUSTON ATLAS (ppm)	DEL MAR (ppm)
RA Test 4 (1/20/81)[b]				
5	222	51	c	99
6	195	24	c	72
7	190	24	16	- 5
8	188	20	16	0
9	171	4	2	- 7
10	179	11	5	3
11	195	24	28	10
12	182	14	17	-95
13	186	22	19	-70
Mean	190	22	15	1
RA Test 4B (1/20/81)[b]				
14	174	1	2	- 97
15	177	5	8	- 92
16	203	25	18	- 31
17	209	24	28	- 28
18	198	15	30	- 33
19	208	29	54	- 31
20	198	21	47	- 33
21	206	27	57	- 43
22	203	27	56	-108
Mean	197	19	33	- 56
RA Test 6 (2/25/81)[d]				
1	285	22	c	c
2	151	16	c	c
3	71	-1	c	c
4	97	6	c	c
5	128	0	c	c
6	168	10	c	c
Mean	150	9	-	-
RA Test 7 (2/25/81)				
1	131	17	c	c
2	281	48	c	c
3	62	20	c	c
4	145	43	c	c
5	203	64	c	c
6	238	67	c	c
7	27	27	c	c
8	12	16	c	c
Mean	137	38	-	-

(Continued)

TABLE 16. RELATIVE ACCURACY TEST RESULTS ON H_2S MONITORS

TEST AND DATE	METHOD 11 RESULTS (ppm H_2S)	DIFFERENCE (Method 11-Monitor) (ppm H_2S)		
		BENDIX (ppm)	HOUSTON ATLAS (ppm)	DEL MAR (ppm)
RA Test 8 (3/31/81)				
1	64	13	c	27
2	116	6	c	42
3	171	16	c	70
4	70	14	c	10
5	115	0	c	26
6	153	-9	c	-2
7	212	-1	c	9
8	77	15	c	4
9	78	12	c	-1
10	84	18	c	9
Mean	114	8	-	19

[a] Fuel gas sample collected in a Tedlar bag taken at this time and analyzed by GC one day later showed less than 2 ppm H_2S.

[b] 30-minute runs.

[c] Monitor not operational.

[d] Fuel gas was spiked with known amount of H_2S for all six runs.

TABLE 17. RESULTS OF COLLABORATIVE RA TEST ON H_2S MONITORS

TIME AND DATE	METHOD 11[a] ($ppm\ H_2S$)		DIFFERENCE (Method 11-Monitor) ($ppm\ H_2S$)					
			BENDIX		HOUSTON ATLAS		DEL MAR	
	LAB 1	LAB 2	LAB 1	LAB 2	LAB 1	LAB 2	LAB 1	LAB 2
RA Test 5 (2/18/81)								
1	23	---	-19	---	-10	---	-27	---
2	28	27	-11	-12	-6	-8	-5	-6
3	51	43	-31	-39	-33	-41	-36	-43
4	43	---	-26	---	-38	---	-35	---
5	41	33	-25	-33	-37	-45	-43	-51
6	33	29	-29	-33	-40	-44	-52	-56
7	32	25	-24	-31	-34	-41	-45	-52
8	31	32	-28	-27	-37	-36	-52	-51
9	29	33	-32	-32	-39	-35	-64	-60
Mean	35	32	-25	-30	-30	-36	-40	-45

[a] The reference method analyses were performed simultaneously by two different laboratories utilizing totally separate equipment, reagents, and standards.

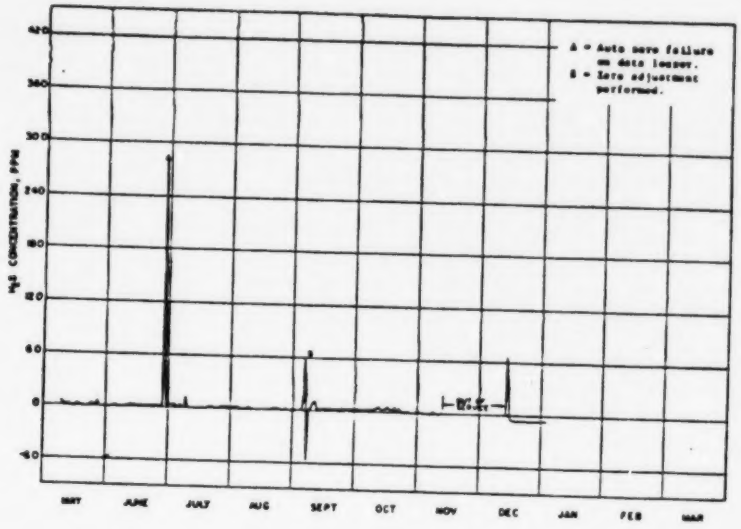

FIGURE 11. ZERO DRIFT TREND FOR BENDIX CEM.

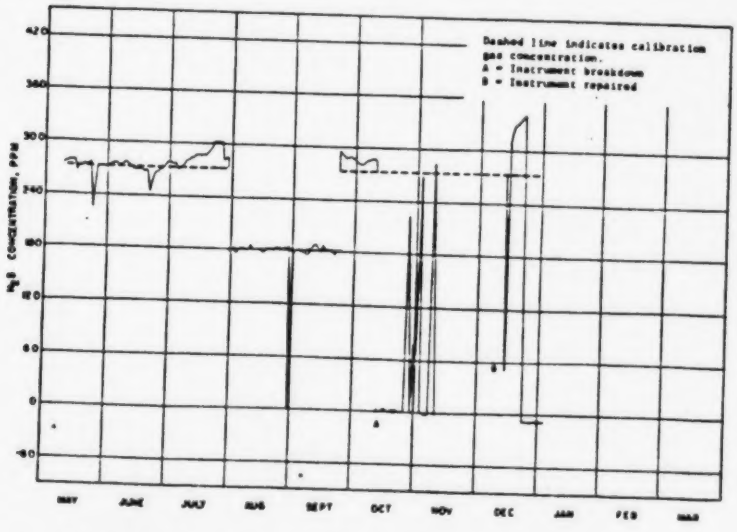

FIGURE 12. SPAN DRIFT TREND FOR BENDIX CEM.

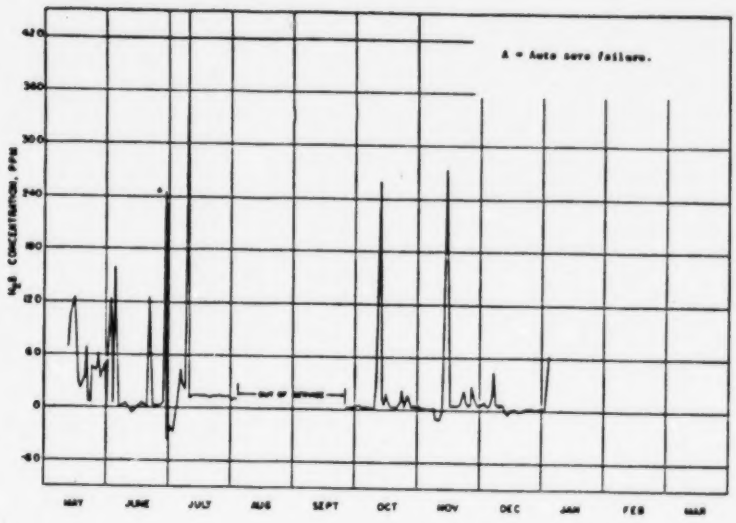

FIGURE 13. ZERO DRIFT TREND FOR HOUSTON ATLAS CEM.

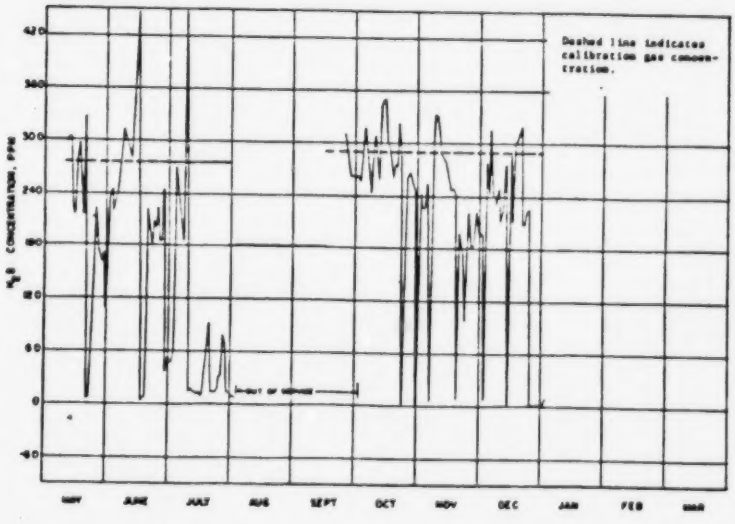

FIGURE 14. SPAN DRIFT TREND FOR HOUSTON ATLAS CEM.

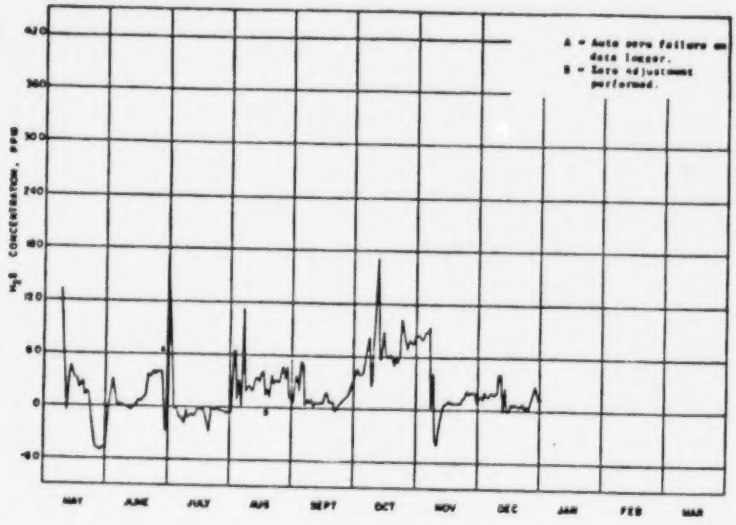

FIGURE 15. ZERO DRIFT TREND FOR DEL MAR CEM.

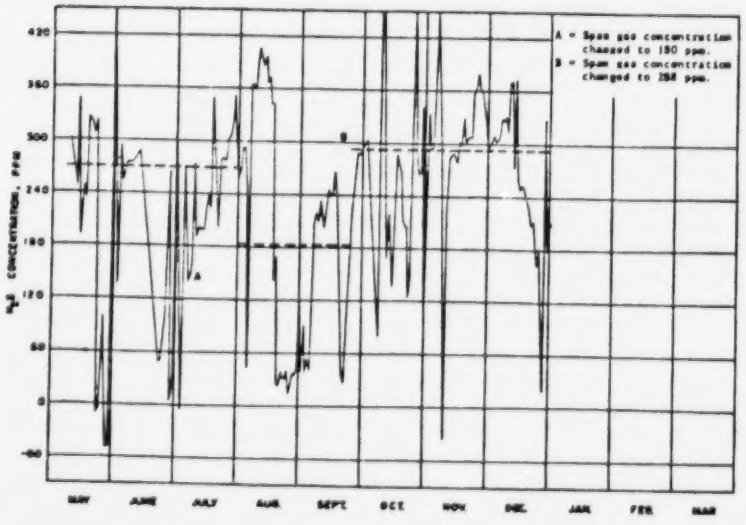

FIGURE 16. SPAN DRIFT TREND FROM DEL MAR CEM.

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APPENDIX A

DEFINITION OF TERMS

Calibration Drift - The difference in the monitor's output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment has taken place.

Calibration Error - The difference between the pollutant concentration indicated by the continuous monitoring system and the known concentration of the test gas mixture.

Interference Equivalent - Positive or negative response caused by a substance other than the one being measured.

Operational Period - A minimum period of time over which a measurement system is expected to operate within certain performance specifications without unscheduled maintenance.

Output Noise - Spontaneous, short duration deviations in the analyzer output that are not caused by input concentration changes. Noise is determined as the standard deviation about the mean expressed as a percentage of full scale.

Precision - Variation about the mean of repeated measurements of the same pollutant concentration, expressed as one standard deviation about the mean.

Range - The minimum and maximum measurement levels.

Relative Accuracy - The degree of correctness with which the continuous monitoring system yields the value of gas concentration of a sample relative to the value given by a defined reference method or the emission standard.

Span Drift - The change in the continuous monitoring system's output over a stated period of normal and continuous operation when the pollutant concentration at the time of measurement is the same known upscale value.

System Response Time - The time interval between a step change in pollutant concentration at the input to the monitoring system and the time at which 95% of the corresponding value is displayed on the system data recorder.

Zero Drift - The change in the continuous monitoring system output over a stated period of time of normal and continuous operation when the pollutant concentration at the time of the measurement is zero.

APPENDIX B

TENTATIVE PLAN FOR THE EVALUATION OF CO AND H_2S CONTINUOUS MONITORS AT REFINERIES

by

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APRIL 1979

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

April 26, 1979

Dear

We are initiating a program to evaluate the long-term reliability of continuous monitors for measuring H_2S in fuel gas feed lines at petroleum refineries and for measuring CO emissions from fluid cat cracker stacks. On March 15, 1978, EPA promulgated a regulation that required petroleum refineries to install such monitors, but only after EPA developed performance specifications for these monitors. The objective of our program is to evaluate tentative specifications recommended for these monitors by an EPA contractor.

The program will involve installing CO and H_2S stack gas monitors at a petroleum refinery and operating and maintaining these monitors for approximately one year. The 1979 Pollution Engineering Yearbook and Product Guide indicates that you may have one or more monitors that could be used in this study. If this is correct, we would appreciate receiving information about your monitor as an aid in planning our program. For your convenience we have enclosed an attachment with this letter that outlines the information that we need.

For your information and comment, I have attached a copy of our tentative plan. We anticipate that the H_2S continuous monitors will be monitoring a stack gas that will be comprised primarily of methane and hydrogen and contain 30-500 ppm H_2S, 10-500 ppm mercaptans and some SO_2. The CO monitors will be monitoring a flue gas that will have the following character: 25-800 ppm CO, 8-15% CO_2; 200-600 ppm SO_2, 200 ppm NO, 8-12% H_2O, and particulate concentrations between 25-150 mg/m^3.

If you wish to submit information about your monitor(s) or need further information, please write to me at the address above or call me at (919) 541-2769.

Sincerely yours,

William J. Mitchell, Ph.D., Chemist
Source Branch
Quality Assurance Division (MD-77)

Attachments

TENTATIVE PLAN FOR THE EVALUATION OF CO AND H_2S CONTINUOUS MONITORS AT REFINERIES

I. BACKGROUND

On March 15, 1978, EPA promulgated New Source Performance Standards that required petroleum refineries to continuously monitor the CO emissions from fluid catalytic crackers and the H_2S levels in fuel gas feed lines. However, at the time the regulations were promulgated, EPA did not have performance specifications available for the CO and H_2S continuous monitors. Therefore, the refineries are not required to install the monitors until these performance specifications are developed.

Tentative performance specifications for both CO and H_2S monitors have now been advanced based on laboratory and field evaluations done by Scott Environmental Technology. In the laboratory phase of Scott's program, candidate instruments were evaluated to determine response characteristics, stability with time, temperature and flow rate, and sensitivity to potential interferences likely present in the stack gas. Instruments that performed adequately in the laboratory were then evaluated at a petroleum refinery to establish their field performance.

Five CO monitors and two H_2S monitors were evaluated at the petroleum refinery during field trials that lasted approximately 55 days. Only one CO monitor and one H_2S monitor performed adequately. In the case of the CO monitors, daily calibration checks were mandatory for reliable operation of the instruments, but even with the inclusion of daily calibration, Scott questioned the long term reliability of these monitors. Instrument malfunctions, sampling system malfunctions and data logger malfunctions plagued these field evaluations.

Based on these studies, Scott proposed tentative performance specifications for both CO and H_2S monitors. The proposed CO monitor specifications are summarized in Table B-1. The proposed H_2S monitor specifications are the same as those described in EPA Performance Specification 2 - "Specifications and Test Procedures for SO_2 and NO_x Continuous Monitoring Systems in Stationary Sources."

TABLE B-1

RECOMMENDED PERFORMANCE SPECIFICATIONS FOR CONTINUOUS MONITORS OF CARBON MONOXIDE AS APPLICABLE TO PETROLEUM REFINERIES

PARAMETERS	SPECIFICATION
Range	0-1000 ppm
Calibration Error	≤2% Span
Relative Accuracy[1]	≤10% Mean Ref. Value
Precision	≤1% Span
Respone Time (System)	≤10 Minutes
Output Noise	≤1% Span
Zero Drift, 2 Hours[1]	≤1% Span
Zero Drift, 24 Hours[1]	≤2% Span
Span Drift, 24 Hours[1]	≤2.5% Span
Interference Equiv. 15% CO_2	≤10 ppm
Interference Equiv. 10% H_2O	≤5 ppm
Operational Period	168 Hours

1 Expressed as sum of absolute mean value plus 95% confidence interval in a series of tests. This value is based on a relative comparison of the monitors to each other and not to Method 10.

II. PROPOSED PLAN

A. Objective

Establish the long-term operational performance (durability/reliability/accuracy) of CO and H_2S monitors when the monitors are installed and maintained as directed by the instrument manufacturer/vendor and from this data determine what are reasonable and useful performance specificaions for those monitors.

B. Duration of Project

The field testing will last approximately one year. The laboratory testing preceding the field study will last one to three months depending on the problems encountered and the instruments selected for evaluation.

C. Site Selection Criteria

The CO monitors will be installed at a fluid cat cracker and the H_2S monitors will be installed on a fuel gas feed line preferably equipped with an amine treater for removal of H_2S. The actual selection of the test site(s) will be made using the following criteria:

1. Attitude of plant management toward program.

2. Accessibility of site to EPA and EPA contractor personnel for installation, calibration and maintenance of equipment.

3. Scheduled plant shut-downs for maintenance, production changes, etc.

4. Availability of a room or trailer that is suitable for installing continuous monitors, i.e., one that can be maintained at a constant temperature and humidity.

5. Availability of a stable, continuous supply of electrical power.

D. Equipment Procurement

1. Continuous Monitors

The continuous monitors will be selected based primarily on engineering judgment about their technical reliability and durability, maintenance requirements, data recording requirements, and availability of spare parts. Specific criteria for monitor selection include the following:

a) Willingness of monitor vendor to cooperate with EPA, e.g., supply the monitoring system requested including all pre-delivery instrument check-outs requested.

b) Cost of the monitoring system to the government in relation to other monitors with similar operating principles.

c) Delivery time involved in obtaining the monitor.

d) Anticipated cost of maintenance, calibration and repair of the instrument including availability of spare parts, ease of on-site repair and availability of service personnel for major equipment repair.

e) Sampling conditions required by the monitor, i.e., temperature, stack gas characteristics, humidity, flow rate, etc., and availability of a suitable sample conditioning system for obtaining the required sampling conditions.

f) Existence of a similar system on other petroleum refineries and the demonstrated performance of the system.

g) Availability and cost of training EPA contractor personnel in the operation and maintenance of the monitoring system.

2. Stack Gas to Monitor Conditioning System

The actual sampling system required to bring the stack gas to the monitors cannot be determined until the field site(s) and the candidate monitors are selected. If a commercially-available system exists that can be obtained at reasonable cost, such a system will be bought. However, if necessary, a site-specific sample conditioning system will be designed and installed by EPA. The system installed will meet or exceed requirements of every monitor that will be used in the evaluation.

3. Data Recording System

It is anticipated that strip chart recorders will be used to record all data generated by the monitors. Data loggers and magnetic tapes will likely not be used since these devices have not demonstrated long-term operational stability. Similarly, manual calibration and span checks will be an integral part of the program rather than relying simply on automatic controllers.

E. Trailer for Housing the Monitors

Monitors require a well-controlled environment for operational stability. A trailer or similar facility that has temperature and humidity controls will be used to house the monitors.

F. Determination of Performance Specifications and Operational Characteristics

The performance of the CO monitors will be compared to the tentative performance specifications now being advanced by QAQPS as Performance Specification 4. The performance of H_2S monitors will be compared to the most recent specifications for SO_2 and NO_x monitors.

Relative accuracy performance tests for CO will be conducted using EPA Method 10 unless ESRL is able to supply a wet chhemical test method for CO. The relative accuracy tests for H_2S will be conducted using EPA Method 11. Initially, the number of samples specified in performance Method 2 for SO_2 will be used for the H_2S and CO relative accuracy tests. Span checks and drift checks will be done daily using calibration gas mixtures that correspond to 0%, 25%, 50%, 75% and 100% of span. However, not all span gases will be used everyday.

Described below is the tentative schedule for these tests. This schedule may change based on final selection of monitors and test sites:

Parameter	Time Interval
Relative Accuracy Test	1 week 1, 2, 4, 8, 12 months
Zero/Span Checks	
0, 50%, 100% span check	daily
0, 25%, 50%, 75%, 100% span check	weekly
Response Time/Noise Check	weekly
Interference of other gases	monthly

G. Tentative Schedule for Accomplishment of Study

Task	Completion Date
Obtain permission to presurvey tentative sites	May 15, 1979
Complete site visits and select test sites	June 15, 1979
Order monitors/sampling systems, etc.	July 15, 1981
Procure necessary supplies for reference method tests	August 15, 1979
Complete laboratory check-out of monitors	November 15, 1979
Install/check-out monitors	January 15, 1980
Complete field studies	January 15, 1981

III. SPECIAL NOTES

A. Each monitor will be subjected to whatever lab tests are necessary to determine if it will work in a field situation. These lab tests may be done by the vendor before shipping the equipment to the EPA contractor.

B. Tentatively, we plan to have the person or persons responsible for maintaining the monitors receive monitor-specific training from the instrument vendor either on-site or at the vendor's facility.

C. Based on cost and anticipated delivery time, spares of those components most likely to fail (phototubes, scrubber columns, switches) will be stored at the test site.

D. If possible, two identical instruments may be operated at the site to yield an estimate of instrument precision. The method of standard additions may also be employed on occasion to check the reliability of the monitors. In this case, a calibration gas would be injected into the sample stream to see if the expected increase in response was obtained.

APPENDIX C

VENDORS RESPONSE TO LETTER FROM EPA

	NO RESPONSE	NEGATIVE RESPONSE CO	NEGATIVE RESPONSE H_2S	PROPOSED INSTRUMENT	COST/OPERATING PRINCIPLE
Applied Automation, Inc Pawhuska Road Bartlesville, OK 74004				CO: Optichrom 102 H_2S: Optichrom 102	CO: $9795/GC/FID H_2S: $13,000/GC/FPD
Astro Ecology Corp. P. O. Box 58159 Houston, TX 77058			XX	CO: 5000	CO: $2800/IR
Bacharach Instruments 2300 Leghorn Street Mountain View, CA 94043	XX				
Baseline Industries P. O. Box 648 Lyons, CO 80540				CO: P 1030A H_2S: P 1030A	CO: $4500/GC/TC H_2S: $3800/GC/FPD
Beckman Instruments, Inc. Process Instruments Division 2500 Harbor Blvd. Fullerton, CA 92634				CO: 865-14 H_2S: 951	CO: $4200/NDIR H_2S: $9000/Chemiluminescence
Bendix Corporation Environmental . . Process Instruments Division P. O. Drawer 831 Lewisburg, WV 24901				CO: 8903 H_2S: 7770	CO: $6000/NDIR H_2S: $9710/GC/FPD
Environmental and Process Analyzer Market Development CEA Instruments, Inc. 15 Charles Street Westwood, NJ 07675		XX	XX		
Calibrated Instruments, Inc. 731 Saw Mill River Road Ardsley, NY 10502	XX				
Contraves-Goerz Corp. 610 Epsilon Drive Pittsburgh, PA 15238	XX				
Control Instruments Corp. 18 Passaic Avenue Fairfield, NJ 07006	XX				
Dictaphone Gas Detection Products Audio/Electronics Division 475 Ellis Street Mountain View, CA 94043	XX				
Digilab, Inc. 237 Putnam Avenue Cambridge, MA 02139			XX	CO: instru. not specified	IR (cost not specified)
E.I. DuPont DeNemours & Co. 1007 Market Street Wilmington, DE 19709		XX		H_2S: 400	H_2S: $8800/UV
Energetics Science, Inc. 85 Executive Blvd. Elmsford, NY 10523			XX	CO: Ecolyzer 3107	CO: $2100/electroch

APPENDIX C

VENDORS RESPONSE TO LETTER FROM EPA

	NO RESPONSE	NEGATIVE RESPONSE CO	NEGATIVE RESPONSE H_2S	PROPOSED INSTRUMENT	COST/OPERATING PRINCIPLE
Dynac [illegible] Envi[illegible] Products Div. Tow[illegible] Road Blue[illegible] PA 19422	XX				
Ecolog Board, Inc. 9257 Independence Ave. Chatsworth, CA 91311	XX				
Ethyl Intertech Corp. 19 Roszel Road Princeton, NJ 08540	XX				
Hewlett-Packard Scientific Instruments Div. 1601 California Avenue Palo Alto, CA 94304	XX				
Horiba Instruments, Inc. 1021 Durvea Ave. Irvine, CA 92714	XX				
Houston Atlas, Inc. 9441 Baythorne Drive Houston, TX 77041		XX		H_2S: 825R-102N H_2S: 722R-102	H_2S: $7200/Pb Ac H_2S: $12,089/PbAc*
Infrared Industries Western Division P O. Box 989 Santa Barbara, CA 93102			XX	CO: 703	CO: $1995/NDIR
Lazar Research Labs, Inc. 509 N. Fairfax Ave. Los Angeles, CA 90036	XX				
Leeds & Northrup Company Sumneytown Pike North Wales, PA 19454	XX				
Melov Laboratories, Inc. 6715 Electronic Drive N. Springfield, VA 22151	XX				
Mine Safety Appliance Co. 600 Penn Center Blvd. Pittsburgh, PA 15235			XX	CO: Lira 202	CO: $6400/NDIR
Monitor Labs, Inc. 10180 Scripps Ranch Blvd. San Diego, CA 92131				CO: Luft detector H_2S: Not specified	CO: $7000/NDIR H_2S: GC/FPD
Process Analyzers, Inc. 1101 State Road Princeton, NJ 08540				CO: 26-222-4 H_2S: 32-230	CO: $6100/GC/TC H_2S: $9900/GC/FPD
Milton Roy Company Flow Control Div. 205 Ivyland Road Ivyland, PA 18974	XX				
Teledyne, Inc. Analytical Instruments Div. 333 L. Mission Drive San Gabriel, CA 91776				CO: 9300 H_2S: 611 DHCO-20X	CO: $9800/NDIR H_2S: $6700/UV
Thermo Electron Corp. Environmental Instruments Div. 108 South Street Hopkinton, MA 01748	XX				

APPENDIX C

VENDORS RESPONSE TO LETTER FROM EPA

	NO RESPONSE	NEGATIVE RESPONSE CO	NEGATIVE RESPONSE H_2S	PROPOSED INSTRUMENT	COST/OPERATING PRINCIPLE
Tracor, Inc. Instrument Division 6500 Tracor Lane Austin, TX 78721	XX				
Western Research and Developers Ltd. 1313 - 44th Ave., NE Calgary Alta Canada		XX	XX		
Del Mar Scientific P. O. Box 486 Addison, TX 75001		XX		H_2S: DN-UVR	H_2S: $4700/PbAc
Anarad, Inc. P. O. Box 3160 Santa Barbara, CA 93105			XX	CO: AR 501R	CO: $3500/NDIR

* Orginally proposed, but when cold ordering Del Mar they offered the 825R-102N.

APPENDIX D

FCC EMISSIONS GAS SAMPLE CONDITIONING SYSTEM

The stack gas was conditioned at the stack to remove particulate, acid mist and moisture. The gas conditioning system was housed in a metal case 55 cm by 76 cm by 33 cm. The system (Figure D-1) consisted of the following parts:

1. Probe. SS 202, length 130 cm, OD 5.1 cm, ID 4.94 cm, slots 2 to 4 cm wide cut in the 40 cm nearest the tip and covered with Balston Type 20/80-A microfiber filter (5.1 cm ID by 45 cm long), glass wool plug in probe tip; and steel plate welded 5 cm from the end to attach probe to port flange and probe extension (Figure D2).

2. Probe Extension. Aluminum pipe, 28 cm long, 10 cm OD, one end welded to aluminum plate (to attach extension to probe) and other end externally threaded to accommodate pipe cap. Each side contained a piece of aluminum tubing 2.5 cm OD by 8 cm long to allow sample to pass from probe into the gas conditioning system and to allow a stack sample to be withdrawn into a Tedlar bag. The bottom of the extension contained a piece of aluminum tubing 1.6 cm OD by 5 cm long for attaching a 60 cm U-shaped drain. This drain continuously removed condensate from the probe extension while maintaining a water seal to prevent ambient air from entering the system.

3. Balston 20/80-A Filter Housing (SS304) with Type 200-80 Grade D and Type 200-35 SS filter support core filter. Gas passed from inside to outside to coalesce water and remove small particulates. A U-trap was attached to the bottom to allow continual draining of the condensate.

4. Balston 97S6 Filter Housing (SS316) with 050-05CH microfiber filters (1.2 cm ID by 3.1 cm long). One of these filters was added to the system December 5, 1980, to reduce plugging of the Perma Pure dryer; the second was added January 9, 1981.

5. Perma Pure Model PD-1000-24S (200 tubes, 60 cm long). Two connected in series to remove moisture. A pressure regulator was used to maintain dryer purge air at a flow of 17 L/min at 2 to 3 psi.

6. Pump. ADI Model 19320-T dual-stage (with Carpenter 20 heads to reduce corrosion), Teflon-coated diaphram and Viton valve gasket and discs. The single-stage pump used originally would be adequate for most systems.

7. Tubing. SS 316 between probe extension and Balston 97S6 filter, polypropylene between 97S6 filter and pump.

8. Sample Line. 200 m long, 0.95 cm ID by 1.2 cm OD, black nylon, unheated.

9. Balston 20/80-A Filter Housing with Type 20/80-A Grade D, microfiber filter. Located immediately in front of the trailer to remove fine particulate.

The overall performance of the gas conditioning system was very good. Problems and changes that occurred between February 11, 1980 and April 28, 1981, are summarized in Table D-1. In general, the following comments are noted:

1. Polypropylene tubing was found to be superior to stainless steel tubing. The latter reacted with the stack gas to yield a fine particulate that collected at bends and elbows in the conditioning system.

2. The Balston 20/80-A filter was difficult to disassemble in the field due to its large diameter and the lack of large wrenches.

3. The U-shaped drains worked well, but care should be taken to prevent freezing; either by wrapping the drain with heating tape or by using heat radiating from the stack.

4. From February 18, 1981, to April 28, 1981, the system worked without failure or maintenance at a sampling rate of 5 to 8 L/min. When disassembled on April 28, 1981, the Perma Pure dryer inlet contained no particulate, the Balston 20/80-A filters were unbroken, the pump inlet diaphram contained a reddish syruplike liquid (pH less than one) that absorbed water rapidly upon exposure to the ambient air. An anion analysis showed that the only anion present was sulfate.

5. The system described was constructed to provide a sample flow rate of 6 to 15 L/min to the trailer with a minimum system response time. For most applications, a flow rate of 1 L/min would be sufficient; thus one PD-750-24 inch (100-tube) Perma Pure dryer might be adequate for

most applications. This would result in a considerable savings. In addition, the probe extension and the Balston 20/80-A filter in the sample case could be replaced with smaller units without adversely affecting the sample conditioning system. Probe filter integrity was maintained as long as the slotted side of the probe was facing downstream. When the probe was rotated 90° so that only half the slotted side of the probe was facing downstream, a hole about one cm in diameter formed in the filter at a point about 35 cm from the tip. A glass wool plug in the probe also helped keep the probe clear.

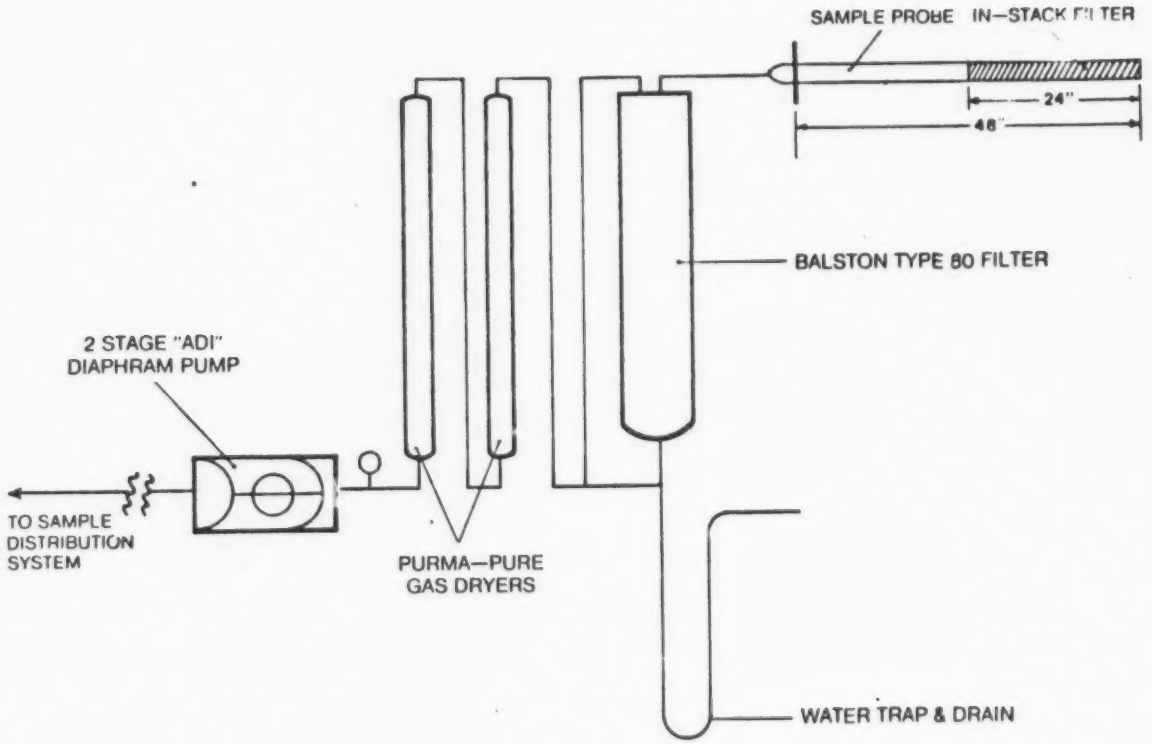

FIGURE D-1. SCHEMATIC DRAWING OF SAMPLE CONDITIONING SYSTEM.

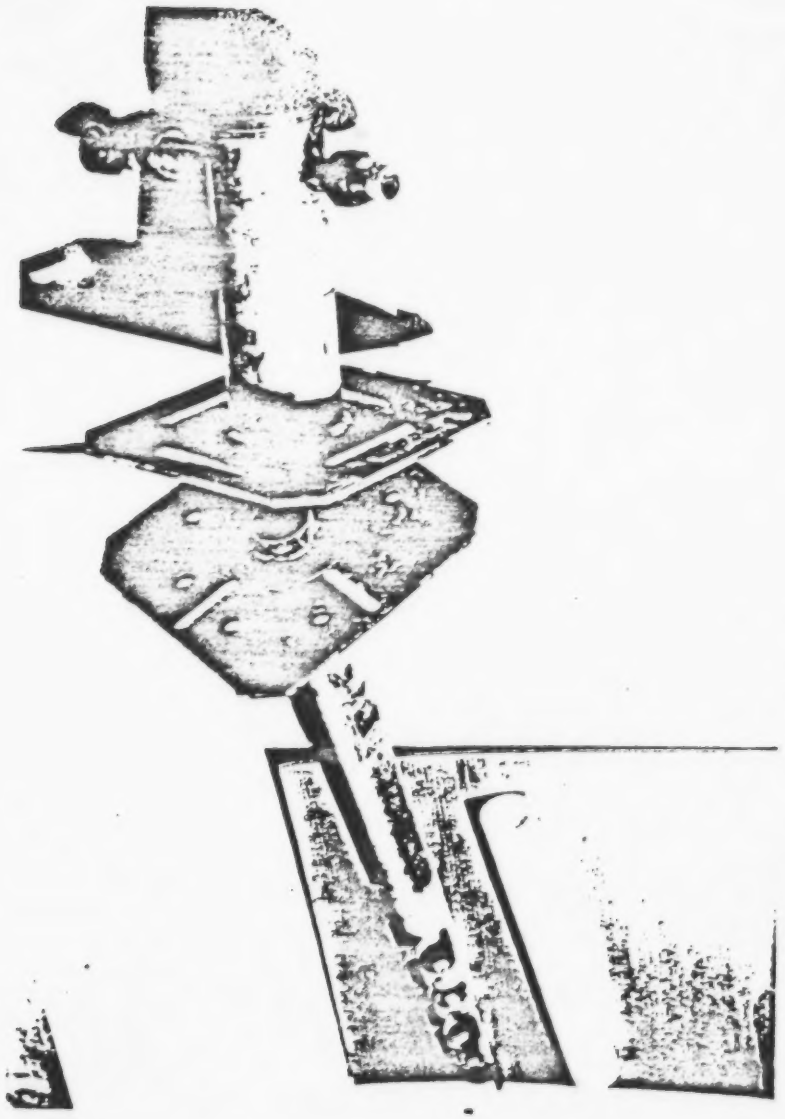

FIGURE D-2. PROBE, PROBE EXTENSION AND BALSTON 20/80-A FILTER.

TABLE D-1. MAINTENANCE/REPAIR OF STACK GAS CONDITIONING SYSTEM OF FCCU

Date	Init. Flow (l pm)	Final Flow (l pm)	Probe/Probe Extension	F-30-1	F-80-1 Drain	F-9756	Perma Pure Dryer	Pump	F-83-2 (at trailer)	PPD Purge Air (l pm)	ACTIVITY:
1980											
2/11	-	6								17	Installed system. Probe slotted side facing downstream with glass wool plug in tip. All SS-316 tubing. Pump single st ADI-19310T with gas recirculation system to control flow.
2/27	3	6						x		17	Flow restricted by fine gray powder at pump inlet. Replaced SS 316 tubing between PPD and pump with polypropylene. CO at pump outlet and in stack 75 ppm by NDIR. Plant monitor read 80 ppm. System leak-checked at 5 inch Hg. Powder analysis: Fe: Ni (7:1); Anion SO_4. pH condensate 2.2. Condensate green.
3/28	6	14	x		x			x		17	Removed pump recirculation system because valve leaking. Put U-trap in to collect condensate. Drain box leaking at sea Rotated probe 90° and removed glass wool plug to see effect on particulate filtering efficiency. Probe clear. CO stack 34 ppm, CO at pump outlet 31 ppm.
4/2	2	12				x				0	PPD purge air line accidently closed off by someone at plant. System full of water but still pumping. Drained system a opened air line.
4/10	9	11						x		18	Put in two stage pump (ADI-19320T) to give 15 psi pressure at trailer to accommodate Applied Automation monitor requirements.
5/30	2	12	x							19	Kinked tubing restricting flow into pump. Replaced cracked probe filter. Probe had small particulate deposit, but was not occluded.
6/3	13	15								17	Plant CO very high. Put in 1:5 dilution system to bring CO into span range of monitor. Dilution system removed August 1980.
7/13	13	13								18	Put aluminum probe extension equipped with U drain onto probe.
9/6										18	System OK. Installed CO_2 monitor in trailer.
9/23	0	12							x	17	Replaced ruptured pump diaphram on pump inlet.
9/29	6	12							x	18	Replaced other pump diaphram, worn but not ruptured. Had green deposit in head.
10/11	-	-								20	Line plugged. Drained 1.5 ℓ from F-80-1 filter. Sample flow meter (rotameter) ball corroded. Removed rotameter from system without replacement.

(Continued)

TABLE D-1. MAINTENANCE/REPAIR OF STACK GAS CONDITIONING SYSTEM OF FCCU

1980										Activity
10/22	0	13						x		Pump inlet plugged with green deposit. Analysis showed: (7:1:1 for Fe:Ni:Cr), anion $SO_4^=$ and NO_3^-, 30% H_2O (by weight). Measured sample flow using PPD purge air rotameter.
11/18	-	-	x				x	x		Probe filter had hole in it. Replaced. PPD partially plugged. Replaced 2 PD 1000-24-SS (61 cm x 200 tubes) with one PD 750-48 (61 cm x 100 tubes). Replaced pump heads (3165S) with Carpenter 20 heads. 50% inlet tubes on both PPD plugged
12/5	-	-	x			x				Hole in probe filter. Placed 9756 filter between F-80-1 and PPD to reduce plugging of PPD.
1981										
1/9	-	-	x							U-drain on probe extension contained frozen condensate. Drained. Replaced 9756 filter, element contained light grey particulate.
1/16	-	-	x	x		x		x		Drain on F-80-1 filter apparently frozen on 1-10-81 allowing condensate to fill system including sampling line. Water froze at night but thawed during day so CO_2 levels during day were normal. Replaced F-80-1 and F-80-2 filters. F-80-1 wet, covered with green slime. F-80-2 covered with grey powder. 9756 filter covered with green/grey powder, replaced filter element.
1/19	-	-	x							Probe filter had hole, replaced and rotated probe so slotted side facing downstream. Put glass wool in probe tip. Put short section of probe filter on exit end of probe, so that it touched the probe extension cap to provide additional filtering.
1/23	-	-								Put tarp over system to utilize stack's radiant heat to prevent freezing of condensate. Put heating tape on probe extension drain.
2/18	25	8						x	x	Purge air regulator had stuck open at 35 psi, tube in dryer ruptured. Some tubes also plugged. Replaced PD 750-48 with a PD 1000-24S PPD. Put two 9756 filters in series. Put Balston 45 G filter downstream of pump and followed with Whitney valve to control flow to 8 lpm.
3/16	6	7								System still functioning. Probe clear. CO_2 stack 12%, CO_2 manifold 12%.
4/28	5	-								System still functioning. CO_2 stack 13%, CO_2 manifold 11%. Removed system.

APPENDIX E

MANUAL METHOD FOR MEASURING CARBON MONOXIDE IN REFINERY GASES

1. PRINCIPLE AND APPLICABILITY

1.1 Principle

An integrated sample is extracted from the gas stream, passed through hydrogen peroxide and alkaline permanganate solutions and collected in a Tedlar bag. The carbon monoxide (CO) concentration in the sample is measured spectrophotometrically using the reaction of CO with a palladium chloride/leuco crystal violet/potassium iodate solution.

1.2 Applicability

This method is applicable for determining CO emissions from stationary sources.

2. RANGE AND SENSITIVITY

2.1 Range. As written, the method applies to gas samples that contain 20 to 1000 ppm CO. Samples containing in excess of 1000 ppm CO can be analyzed by reducing either the gas volume or the shaking time. Samples containing less than 20 ppm can be analyzed by increasing the volume of sample reacted with the palladium chloride/leuco crystal violet/potassium iodate solution or by increasing the shaking time or frequency. However, if such changes are made in the procedure, the linearity of the absorption curve must be checked under these conditions.

2.2 Sensitivity. Sensitivity depends on shaking time, shaking frequency, gas volume and shape of reaction vessel and cannot be specified absolutely. As written, the sensitivity of the method is approximately 10 ppm CO.

2.3 Interfering Agents. Sulfur oxides, nitric oxide, and other acid gases which interfere with the reaction, are removed from the gas sample during sample collection. These gases are removed by passing the sampled gas through a 4 percent potassium permangate/5-percent sodium hydroxide solution. Carbon dioxide does not interfere with the reaction, but, because it is removed by the scrubbing solution, its concentration must be measured and an appropriate volume correction made.

4. PRECISION, ACCURACY AND STABILITY

4.1 Precision. The estimated intralaboratory standard deviation of the method is 2.5 percent of the mean for gas samples analyzed in triplicate. This estimate, which applies to the concentration range 20 to 1000 ppm, was determined from 22 samples collected at a petroleum refinery. The interlabortory precision has not been established.

4.2 Accuracy. On the average, the manual method results were biased 4 percent high for 22 samples analyzed by an NDIR calibrated with NBS standards. The manual method was biased 5 percent high when used to analyze certified calibration gas mixtures that contained SO_2, NO, CO_2, and 100 to 500 ppm CO in nitrogen.

4.3 Stability. The individual components of the colorimetric reagent are stable for at least one month, but the colorimetric reagent must be used within 3 hours after preparation to avoid excessive blank correction. For optimum accuracy the samples must be reacted and analyzed no later than 3 hours after the colorimetric reagent has been prepared.

5. APPARATUS

5.1 Sampling (Figure E-1)

5.1.1 Probe. Stainless steel, sheathed Pyrex glass or equivalent, equipped with a glass wool plug to remove particulate matter.

5.1.2 Impinger. Three Greenburg-Smith impingers connected in series with leak-free connections.

5.1.3 Pump. Leak-free pump, Metal Bellows Model 110 or equivalent with stainless steel and Teflon parts to yield a flow rate of 0.2 to 0.4 L/min.

5.1.4 Surge Tank. Installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter.

5.1.5 Rate Meter. Calibrated rotameter, or equivalent, to measure flow rates between 0 to 0.4 L/min.

5.1.6 Flexible Bag. Tedlar, or equivalent, with a capacity of 10 liters. Bag must be leak-free.

5.1.7 Valve. Needle valve, or equivalent, to adjust flow rate.

5.1.8 Fyrite Analyzer, or equivalent, to measure CO_2 concentration to within $\pm$0.5 percent accuracy.

5.2 Analytical

5.2.1 Spectrophotometer. Single or double beam to measure absorbance at 589 nm. Slit width should not exceed 20 nm.

5.2.2 Vacuum Gauge. U-tube manometer, 1 meter (36 in.), with 1-mm divisions, or other gauge capable of measuring pressure to within ±2.5 mm Hg (0.10) in. Hg).

5.2.3 Pump. Capable of evacuating the gas reaction bulb to a pressure equal to or less than 75 mm Hg (3 in. Hg) absolute, equipped with coarse and fine flow control valves.

5.2.4 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) must be requested. An adjustment for elevation differences between the weather station and sampling point must then be made at a rate of minius 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase, or vice versa for elevation decrease.

5.2.5 Reaction Bulbs. Pyrex glass, 100-125 mL with Teflon stopcock, leak-free at 650 mm Hg. Designed so that 10 mL of the colorimetric reagent can be added and removed easily and accurately (Figure E-2). Commercially available gas sample bulbs such as Supelco #2-2161 and Alltech #7012 can also be used.

5.2.6 Volumetric Pipettes. Class A, 4 mL and 10 mL and 1 mL graduated pipette.

5.2.7 Volumetric Flasks. 100 mL

5.2.8 Graduate Cylinder. 1000 mL.

5.2.9 Shaker Table. Reciprocating-stroke type such as Eberback Corp. Model 6015. A rocking arm or rotary-motion type shaker may also be used. The shaker must be large enough to accommodate at least six gas sample bulbs simultaneously. It may be necessary to construct a table top extrusion for most commercial shakers to provide sufficient space for six bulbs (Figure E-3).

5.2.10 Spectrophotometer cells. 1 cm pathlength.

6.0 REAGENTS

6.1 Sampling

6.1.1 Alkaline Permanganate Solution. Prepare by dissolving 40 grams of ACS reagent grade sodium hydroxide and 50 grams of ACS reagent grade potassium permanganate in 1 liter of distilled water. This is sufficient for removing NO and SO_2 from 50 liters of gas containing 15% CO_2.

6.2 Analysis

6.2.1 Stock Solutions

6.2.1.1 Potassium Iodate. ACS reagent grade, or equivalent.

6.2.1.2 Sodium Chloride. ACS reagent grade, or equivalent.

6.2.1.3 Palladium Chloride. ACS reagent grade, or equivalent.

6.2.1.4 Sodium Monohydrogen Phosphate Heptahydrate ($Na_2HPO_4 \cdot 7H_2O$). ACS reagent grade, or equivalent.

6.2.1.5 Leuco Crystal Violet (4,4',4" methylidynetris (N,N-dimethylaniline)). Eastman Kodak Company Stock No. 33651.

6.2.1.6 Phosphoric Acid (85%). ACS reagent grade, or equivalent.

6.2.2 Working Solutions

6.2.2.1 Sodium Monohydrogen Phosphate (0.001M). Dissolve 2.68 grams in 100 mL of distilled, deionized water. This solution is stable indefinitely.

6.2.2.2 Sodium Tetrachloropalladate(II) Solution (0.005M). Dissolve 0.0887 grams of palladium chloride and 0.0595 grams of sodium chloride in 50 mL distilled, deionized water and dilute to 100 mL. This solution is stable for at least one month. If a brown precipate forms it can be dissolved by adding a few crystals of sodium chloride.

6.2.2.3 Leuco Crystal Violet Solution. Dissolve 0.0256 grams leuco crystal violet in 80 mL water containing 10 mL of 85% phosphoric acid and dilute to 100 mL. This solution is stable for at least one month.

6.2.2.4 Potassium Iodate Solution (0.1M). Dissolve 2.14 grams of potassium iodate in 100 mL of distilled deionized water. This solution is stable indefinitely.

6.2.2.5 Colorimetric Solution. Pipet 4.0 mL each of potassium iodate solution (6.2.2.4), leuco crystal violet solution (6.2.2.3) and sodium tetrachloropalladate (II) solution (6.2.2.2) into a 100 mL volumetric flask. Pipet 0.6 mL sodium monohydrogen phosphate solution (6.2.2.1) into the flask and dilute to volume. This solution should be used within 3 hours of preparation to minimize the contribution of the blank and the sample absorbance. This is sufficient volume to analyze three stack gas samples in triplicate.

6.2.2.6 Standard Gas Mixtures. Traceable to NBS standards and containing between 100 and 1000 ppm CO in nitrogen. The calibration gases shall be certified by the manufacturer to be within ± 2 percent of the specified concentration.

7.0 PROCEDURE

7.1 Sampling. Evacuate the Tedlar bag completely using a vacuum pump. Assemble the apparatus as shown in Figure E-1. Loosely pack glass wool in the tip of the probe. Place 400 mL alkaline permanganate solution (6.2.1) in the first two impingers and 250 mL in the third. Connect the pump to the third impinger and follow this with the surge tank and the rate meter. Do not connect the Tedlar bag to the system at this time.

Leak-check the sampling system by plugging the probe inlet and observing the rate meter for flow. If flow is indicated on the rate meter, do not proceed further until the leak is found and corrected. Insert the probe into the stack and draw sample through the system at 300 ± 50 mL/min for 5 minutes. Connect the evacuated Tedlar bag to the system, record the time and sample for 30 minutes, or until the Tedlar bag is nearly full. Record the sampling time, the barometric pressure and the ambient temperature. Purge the system as above immediately before each sample.

The sampling system above is adequate for removing sulfur and nitrogen oxides from 50 liters of stack gas when the concentration of each is less than 1,000 ppm and the CO_2 concentration is less than 15%. The samples in the Tedlar bag should be stable for at least one month, if the bag is leak-free.

7.2 Ancillary Methods

Measure the CO_2 content in the stack to the nearest 0.5% each time a CO bag sample is collected. A grab sample analyzed by the Fyrite analyzer is acceptable.

7.3 Analysis

Assemble the system shown in Figure E-4 and record the information required in Table E-1 as it is obtained. Pipet 10.0 mL of the colorimetric reagent (6.2.2.5) in each gas reaction bulb (5.2.5) and attach the bulbs to the system. Open the stopcocks on the gas bulbs but leave the valve on the Tedlar bag closed. Turn on the pump, fully open the coarse-adjust flow valve and slowly open the fine-adjust valve until the vacuum is at least 550 mm Hg. Now close the coarse adjust valve and observe the manometer to be certain that the system is leak-free. Wait a minimum of two minutes and if the pressure has decreased less than 1 mm, proceed as described below. If a leak is present, find and correct it before proceeding further.

Record the vacuum pressure to the nearest 0.1 mm Hg and close off the gas bulb stopcock. Open the Tedlar bag valve and allow the system to come to atmospheric pressure. Close the bag valve, open the pump coarse adjust valve and evacuate the system again. Repeat this fill/excavation procedure at least twice and then close off the pump coarse adjust valve, open the Tedlar bag valve and let the system fill to atmospheric pressure. Open the stopcocks on the gas bulbs and let the entire system come to atmospheric pressure. Close the gas bulb stopcocks, remove the bulbs and place them on the shaker table with their main axis either parallel to or perpendicular to the plane of the table top.

Record the room temperature and the barometric pressure (nearest 0.1 mm Hg) after each set of gas bulbs is filled. At least one set of bulbs from a Tedlar bag containing a known concentration of CO in nitrogen must be used each time a set of samples is shaken. Improved accuracy will be obtained if two standards are included each time. Also, to avoid cross contamination of samples, the bulb filling system must be purged with ambient air for several minutes between samples.

Shake the samples for 25 minutes if the expected concentration is less than 600 ppm and for 20 minutes if it is between 600 and 1,000 ppm. Place the contents of each bulb in a labeled test tube or other suitable vessel.

Measure the absorbance of each sample at 589 nm using water as the reference; also measure the absorbance of the unreacted colorimetric reagent used for that set of samples to serve as a reagent blank. Reject the analysis if the blank absorbance is greater than 0.1.

The absorbance curve is linear to an absorbance of 1.8. If the sample absorbance exceeds this, the sample can be diluted with the colorimetric reagent.

The reaction between CO and the colorimetric solution is slow. For example, unshaken samples set aside one hour after filling show no significant absorbance.

8.0 CALIBRATION AND QUALITY ASSURANCE

8.1 Gas Bulb Calibration

Weigh the empty bulb to the nearest 0.1 gram. Fill the bulb with distilled water and again weigh to the nearest 0.1 gram. Subtract the tare weight and calculate the volume in liters to three significant figures using the density of water (at the measurement temperature). Record the volume on the bulb or, alternately, etch an identification number on the bulb and record the volume in a notebook.

8.2 Rate Meter Calibration

Assemble the system as shown in Figure E-1 (the impingers may be removed) and attach a volume meter to the probe inlet. Set the rotameter at 300 mL/min, record the volume on the volume meter, start the pump and pull gas through the system for 10 minutes. Record the final volume on the volume meter and determine the volume of gas that passed through the system. Repeat this procedure for at least two other flow rates between 100 and 500 mL/min and prepare a calibration curve for the rate meter.

8.3 Spectrophotometer Calibration

The calibration curve is established for each batch of samples shaken at the same time by running standards along with the stack samples. For highest accuracy two sets of standards should be run, but acceptable results have been obtained when only one set of standards was used per batch of samples.

8.4 Quality Assurance

8.4.1 System Shaking Time

Before field samples are analyzed, the linearity of the absorption curve as a function of shaking time must be established for the analytical system. This can be accomplished as follows: Fill a Tedlar bag with a CO concentration at least as high as the highest level expected to be encountered in the field samples. Fill at least six gas bulbs with gas from the bag as described in Section 7.3 and set them on a shaker. After shaking has been initiated remove two bulbs at 15 minutes, two at 30 minutes and two at 60 minutes and measure the absorbance of each solution. Calculate the absorbance per

volume of gas (SA) according to Equation E-1 (Section 9.2) for each sample and determine the average SA for all samples with identical shaking times. Plot this average SA versus the shaking time to determine the line of best fit or the attainment curve. Use this data to determine the shaking time and sample volume required for sample analysis.

8.4.2 Sample Bag-Leak Checks

While a bag-leak check is required subsequent to sample collection, it should also be done before the bag is used for sample collection. The bag should be leak-checked in the laboratory and will be used according to the following procedures. Connect the bag to a water manometer and pressurize the bag to 5 to 10 cm H_2O (2 to 4 inches H_2O). Allow the bag to stand for 60 minutes. Any displacement in the water manometer indicates a leak. Now evacuate the bag with a leakless pump that is connected on the downstream side to a flow indicating device such as a 0 to 100 mL/min rotameter or an impinger containing water. When the bag is completely evacuated, no flow should be evident if the bag is leakless.

9.0 CALCULATIONS

9.1 Abbreviations and Symbols

SA = Sample absorbance per volume of gas in bulb
CO_{Bag} = Concentration of CO in Tedlar bag (ppm, dry basis)
CO_{Stack} = Concentration of CO in stack (ppm, dry basis)
FCO_2 = Volume fraction of CO_2 in stack
B_W = Moisture content of gas in bag

9.2 Calculation of CO

9.2.1 Calculation of SA

Calculate the sample absorbance per volume of gas (SA) for each gas bulb (Equation E-1) and record the value in Table E-1. Calculate the average SA for each bag sample and compare the three values to the average. If any single value differs by more than 10 percent from the average, reject this value and calculate a new average using the two remaining values.

$$SA = \left[\frac{\text{Sample Absorbance Corrected for Blank}}{\text{Bulb Volume - Volume Reagent}}\right]\left[\frac{\text{Barometric Pressure}}{\text{Sample Pressure in Bulb}}\right] \quad \text{(E-1)}$$

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9.2.2 Calculation of CO Concentration in Bag

9.2.2.1 Single Standard Shaken with Samples

Calculate the CO concentration in the bag using Equations E-2 and E-3. If condensate is visible in the Tedlar bag, calculate B_w using Table E-1 for the temperature and barometric pressure in the room where the analysis was done. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{\text{Vapor pressure of water in bag}}{\text{Barometric pressure}} \qquad \text{(E-2)}$$

$$CO_{Bag} = \left[\frac{\text{ppm CO in std}}{1-B_w}\right]\left[\frac{\text{Average SA sample}}{\text{Average SA std}}\right] \qquad \text{(E-3)}$$

9.2.2.2 Two Sets of Standards Shaken with Samples

Construct a graph of concentration versus the average SA for each standard forcing the curve through the origin. Determine the CO concentration in each Tedlar bag stack sample using the average SA for each sample and correct for the amount of moisture present (B_w).

9.2.3 Calculation of Stack CO (dry basis)

Calculate the CO in the stack using Equation E-4.

$$CO_{Stack} = CO_{Bag}\,(1-F_{CO_2}) \qquad \text{(E-4)}$$

10.0 BIBLIOGRAPHY

Lambert, J.L., and R.E. Weins. Induced Colorimetric Method for Carbon Monoxide. Anal. Chem., 46: 929-930, 1974.

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TABLE E-1. MOISTURE CORRECTION

TEMPERATURE (^{o}C)	VAPOR PRESURE H_2O (mm Hg)
4	6.1
6	7.0
8	8.0
10	9.2
12	10.5
14	12.0
16	13.6
18	15.5
20	17.5
22	19.8
24	22.4
26	25.2
28	28.3
30	31.8

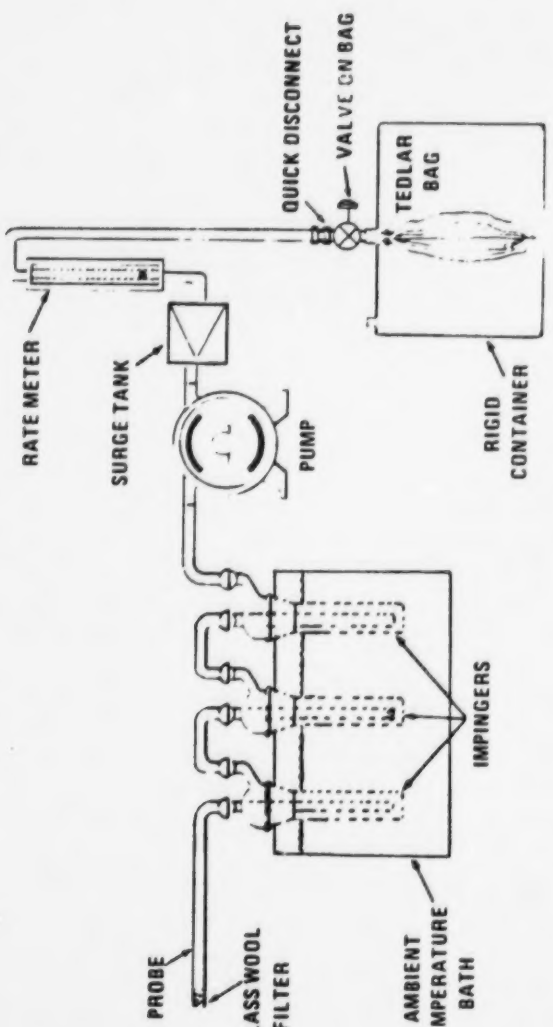

FIGURE E-1. CO SAMPLING TRAIN

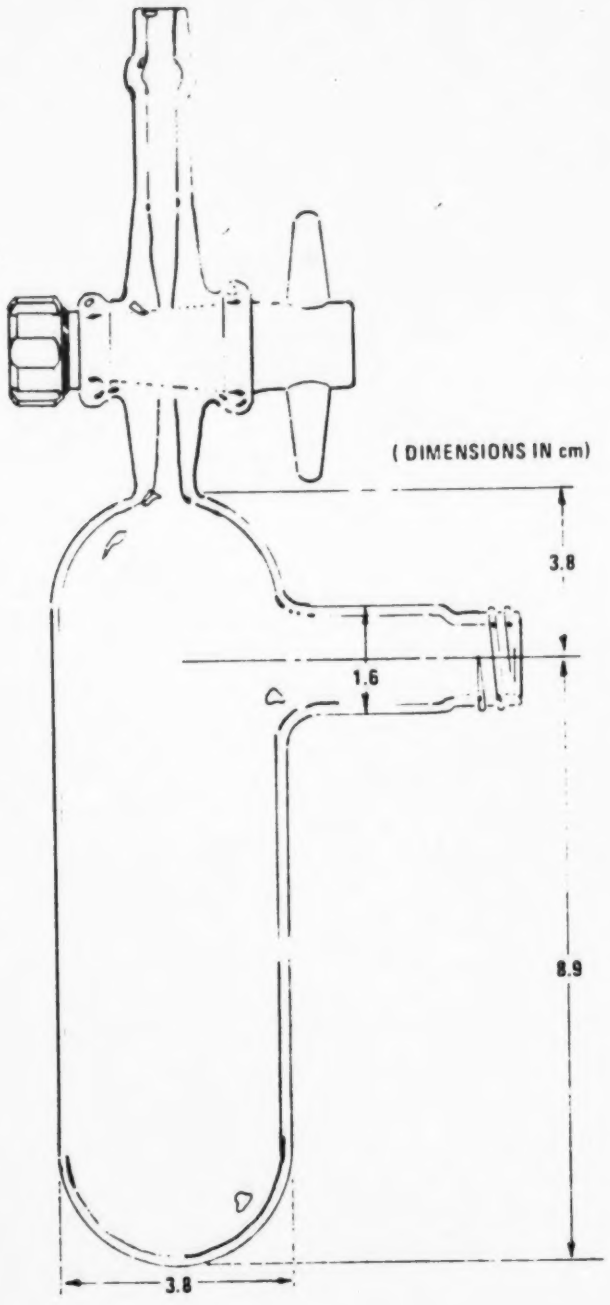

FIGURE E-2. GAS REACTION BULB (0.1 liter)

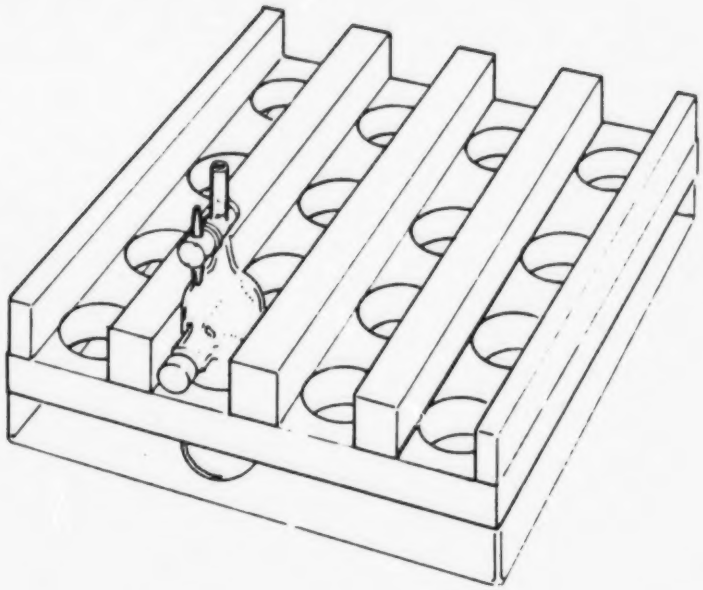

FIGURE E-3. ADAPTOR FOR HOLDING GAS BULBS ON SHAKER TABLE

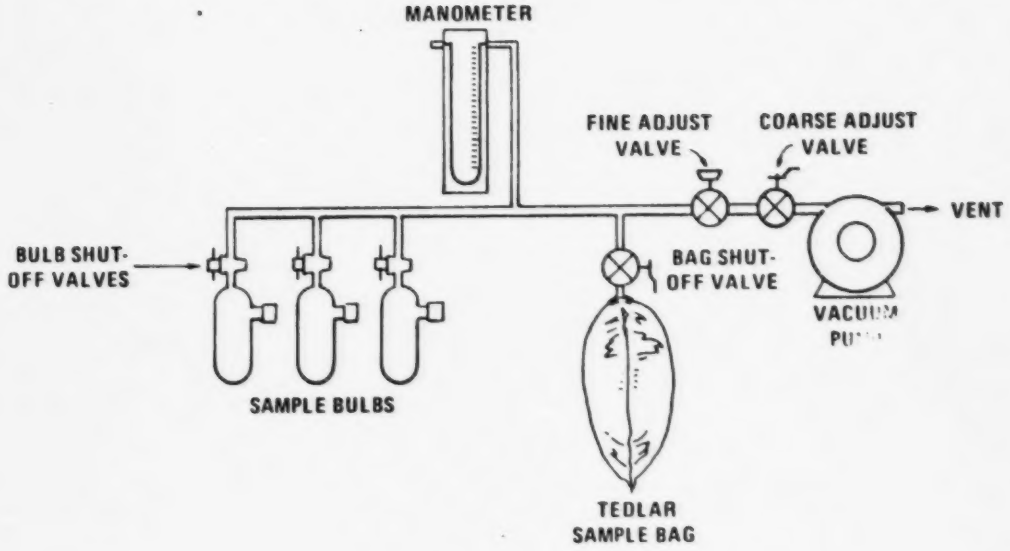

FIGURE E-4. GAS BULB FILLING SYSTEM

TABLE E-2. DATA RECORDING SHEET FOR SAMPLES ANALYZED IN TRIPLICATE

SAMPLE NO./ TYPE	ROOM TEMP. (°C)	STACK Σ CO	BULB NO.	BULB VOL. (L)	VOL. REAGENT IN BULB (L)	PARTIAL PRESSURE OF GAS IN BULB (mm Hg)	BAROMETRIC PRESSURE (mm Hg)	SHAKING TIME (min)	Abs VERSUS WATER	SAMPLE Abs CORRECTED FOR BLANK	SAMPLE Abs/L (SA)	AVG. (SA)
Blank												
Std. 1												
Std. 2												
Sample 1												
Sample 2												
Sample 3												

APPENDIX F

INSTRUMENT EVALUATION HISTORY

APPLIED AUTOMATION OPTICHROM 102

1/4/80	Instrument received with no instruction manual.
1/22/80	Instruction manual received, started wiring instrument.
2/2/80	Power supply failed.
2/4/80	New power supply failed.
3/10/80	Incorrect output found (overloaded). Power supply failed.
3/31/80	Serviceman from Applied Automation arrived to repair instrument.
4/2/80	Instrument repaired, power supply, output board and temperature controller replaced.
4/3/80	Output is negative.
4/10/80	Output problem fixed by reversing wiring to output board and by moving a resistor on it to another position.
4/16-4/17/80	Transported to refinery in trailer.
4/21/80	Instrument turned back on.
4/25/80	Fuse blew in heater circuit.
6/9/80	Zero response varying badly.
7/3/80	Negative peak before CO peak on chromatogram detected. Chromatograms sent to manufacturer as aid in troubleshooting.
9/18/80	Condensation in FID caused corrosion to internal parts. Monitor shut off until manufacturer's service representative call.
11/10-11/12/80	Applied Automation serviceman tried to repair monitor - was unsuccessful. Monitor shut down.

ECOLYZER 3107

10/18/79	Instrument received. Checked out. No problems found in laboratory checkout.
4/16-4/17/80	Transported to refinery in trailer.
4/21/80	Instrument turned on.
4/27/80	Model 2949 filter failed. Replaced.
4/28/80	Model 2949 filter failed. Replaced.

5/3/80	Model 2949 filter failed. Replaced.
5/80	Large carbon filter [illegible] to monitor sample line (replaces Model [illegible] filter) to extend operation time.
9/[illegible]/81	Electrochemical cell going bad. Span control was unable to span monitor.
1/17/81	New electrochemical cell installed, monitor zeroed and spanned.
2/17/81	Model 2949 filter failure caused electrochemical cell to fail. Monitor removed from evaluation.

ANARAD 501-R

10/2/79	Instrument received and checked out in laboratory without problems.
4/16-4/17/80	Transported to refinery in trailer.
4/21/80	Instrument started up. No problems or outages occurred before testing was completed in April 1981.

MSA LIRA 202

11/2/80	Instrument not operational as received.
1/14/80	Put into operation.
2/27/80	Apparent failure of output board. Output had worked previously (on PD-2064) but output now less than 4 mA. Called MSA. New output board ordered.
3/3/80	New output board arrived, installed. Output still not correct. MSA suggested checking output by voltage drop across a resistor. Output seemed to be okay by this method, but power supply board failed soon after test.
3/4/80	Ordered new power supply. MSA suggested that output problem could be solved by installing a matching circuit between the MSA instrument and the data logger.
3/11/80	Power supply board arrived.
3/10-4/3/80	Electronics expert, R. Burdine, made several visits to ascertain output problem and built a circuit to correct problem. His conclusion was that such a circuit was not needed, but that output board was bad (again). New board ordered.
4/15/80	New board arrived, not tested (trailer packed for moving).
4/16-4/17/80	Transported to refinery in trailer.
4/21/80	Instrument started up. Output still bad.
4/21-5/1/80	Instrument off. MSA contacted from Auburn.

5/1/80	D. Tiskiewic of MSA came to check problem. According to his meter, output was 4-20 mA.
5/2/80	Mr. Tiskiewic said that matching circuit was needed. MSA-Pittsburgh would find and send one.
5/3-5/20	Instrument off. No word on matching circuit.
6/3/80	Matching circuit received and installed by MSA serviceman.
6/9-6/16/80	Lab evaluation completed in field.
9/18/80	Span and zero adjustment not possible. Complete optical alignment restored performance. Instrument continued to operate normally throughout the remaining part of the evaluation.

TELEDYNE 611 DMCO-20X

2/80	Instrument received with no instructions on how to install or use molecular sieve canisters.
3/13/80	Initial setup and adjustment. Dimensional instability noted: very sensitive to even the slightest change of attitude with respect to horizontal - even microscopic changes significant.
4/16-4/17/80	Transported to refinery in trailer.
4/21/80	Instrument turned on and interference in fuel gas noted.
4/29/80	Molecular sieve installed on sample line. No effect on sample concentration. Impossible to zero and span instrument.
5/1/80	Molecular sieve removed.
5/7/80	2-hour drift RA Test spoiled by very high sample concentration. Instrument readout did not change before, during or after period of high concentration.
9/18/80	Monitor shut off due to lack of reliable data caused by interference.
11/2/80	Molecular sieve received from Teledyne. When installed, no startup was possible because of optical system failure.

BENDIX 7770

1/3/80	Instrument received.
2/14/80	Connections to gas services made, instrument started up. Several tube fittings inside leaked and had to be tightened. Initial adjustment made (oven temp, flows, etc.).

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3/11/80	Internal plumbing modified to accept separate sources for valve and heater air. When instrument was restarted, oven heater was inadvertently shorted causing destruction of TRIAC in heater control circuit. New TRIACs ordered.
3/21/80	Parts received but proved to be wrong. Correct parts ordered.
4/1/80	Correct parts received, installed successfully. Instrument restarted.
4/16-4/17/80	Transportation to refinery in trailer.
4/21/80	Instrument started back up.
5/7/80	2-hour drift RA Test spoiled due to high H_2S. Instrument system recovered from high H_2S in about 4 hours.
11/5/80	Monitor failure from 2 weeks previous caused by diaphragm on sample valve. New part ordered.
12/15/80	Diaphragm replaced. Monitor operating properly.
2/25/81	Sample valve diaphragm ruptured and repaired. Instrument operated properly throughout the remaining field evaluation.

DEL MAR SCIENTIFIC DM-W

2/10/80	Monitor received and set-up.
4/16-4/17/80	Transported to refinery in trailer.
4/21/80	Instrument turned on. Pressure/flow problems noted. Sensitivity critically dependent on flow (which varies with pressure and gas viscosity).
5/7/80	Very high H_2S concentration encountered in fuel gas at 10:00 am. Analyzer did not recover until next day. Instrument operated properly throughout study, but gas dilution system was not appropriate for fuel gas dilution.

HOUSTON ATLAS 825/102R

12/14/79	Instrument received.
1/20/80	Instrument setup.
4/16-4/17/80	Transported to refinery in trailer.
4/21/80	Instrument turned on. Output overloads data logger. Tape does not advance. Ordered new output/cycle time board.
4/23/80	New board arrived. No effect. Timer relay ordered.

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4/[illegible]/80	Relay received. No effect.
5/1/80	Abraham Asperic of HAI arrived to troubleshoot. Did not find problem. Took analyzer back.
5/5/80	Asperic informed us of wiring mistake to data logger. Sent instrument back to us.
5/8/80	Instrument arrived with wiring instructions.
5/8/80	Instrument turned on - works.
9/11/80	Monitor sent to manufacturer for repair.
9/18/80	Monitor returned by manufacturer.
11/2/80	Houston Atlas serviceman found cause of drift to be condensation in vent line.
1/6/81	Dilution system breakdown. Circuit board installed backwards by contractor personnel. New part delivered.
3/31/81	Monitor failure due to corrosion in timer.

PROCESS ANALYZERS INCORPORATED 32-230

12/20/79	Instrument received.
1/80-3/80	Instrument not operational - many circuit cards exchanged with manufacturer. Instrument eventually returned for repair.
5/9/80	Monitor returned from manufacturer allowed to warmup until next site visit.
6/9/80	Monitor broken down during 1-month warmup. Returned to manufacturer.
8/28/80	Monitor returned to manufacturer.
9/18/80	Monitor returned to field test, 4 to 20 mA output not functioning.
10/1/80	Monitor stopped operating.
11/5/80	Monitor failure caused by wearout of 10 port valve. Monitor shut down and removed from further testing.

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